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Analysis of Aldehydes and Ketones in the Gas Phase

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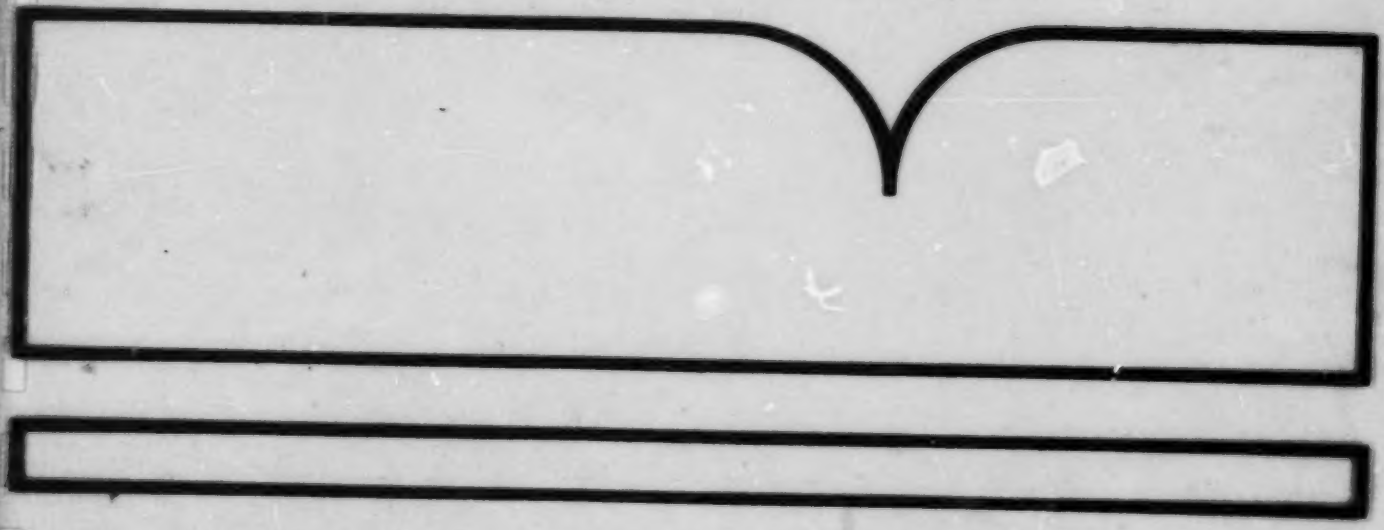

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ANALYSIS OF ALDEHYDES AND KETONES IN THE GAS PHASE

by

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The development and testing of a 2,4-dinitrophenylhydrazine-acetonitrile (DNPH-ACN) method for the analysis of aldehydes and ketones in ambient air are described. A discussion of interferences, preparation of calibration standards, analytical testing, fluorescence methods and cartridge sampling are discussed. The results of atmospheric sampling in an urban area and atmospheric and cloudwater sampling in a rural area are included.

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Abstract

Carbonyl compounds, and in particular, aldehydes and ketones are important constituents of photochemical smog. They are emited in automotive exhaust and are produced during, and play a role in, the photooxidation of organic compounds in the lower atmosphere. Because of the key role of aldehydes and ketones in atmospheric chemistry their analysis has received considerable attention. In the report are discussed some of the details of the testing and use of the DNPH-ACN methods for the determination of aldehydes in ambient air. Included are: a discussion of interferences, the preparation of calibration standards, HPLC column evaluation, analytical testing, dicarbonyl-DNPH analysis, fluorescence methods, preliminary cartridge testing, and the results of atmospheric sampling in Schenectady, NY and atmospheric and cloudwater sampling on Whiteface Mtn. in Wilmington, NY. The method is found to be efficient and accurate for urban use but may not be suitable for "clean" air sampling for aldehydes other than formaldehyde.

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Chapter 1

Introduction

Carbonyl compounds, and in particular, aldehydes and ketones are important constituents of photochemical smog.[1] They are emited in automotive exhaust, are produced during, and play a role in, the photooxidation of organic compounds in the lower atmosphere and they are active participants in free radical chain reactions. Modern computer models simulating the chemical reactions in urban atmospheres require a knowledge of formaldehyde and other aldehyde concentrations.[2]

Because of the key role of aldehydes and ketones in atmospheric chemistry their analysis has received considerable attention.[3] Standard methods have also been adopted for the determination of total aldehydes using 3-methyl-2-benzothiazolone (MBTH) and for formaldehyde specifically using chromotropic acid as colorimetric reagents.[4] Detailed analysis of the aldehyde composition of air samples has been reported using 2,4-dinitrophenylhydrazine (DNPH) derivatization followed by GC analysis.[5]

Recent advances in high performance liquid chromatography (HPLC) techniques have prompted the development of a number of methods that depend on derivatization of the aldehydes and then HPLC separation of the derivatives. The reversed phase separation of the DNPH aldehyde derivatives was first reported by Kuwata and coworkers.[6] Their procedure involved trapping the aldehydes as their DNPH derivatives in aqueous solution and extraction of the derivatives and HPLC analysis, with uv absorption detection at 254 nm. This author developed a modification of their procedure. The modification involved DNPH derivatization in acetonitrile (ACN) solution that removed the necessity for extraction of the DNPH derivatives. In addition, the sensitivity of the method was increased by using absorption detection at 360 nm.[7] An additional extraction method based on DNPH derivatization followed by HPLC analysis and uv detection has also been proposed.[8] Another more recent development by Swarin and Lipari at General Motors Research Laboratory involves the use of 2-diphenylacetyl-1,3-indandione-1-hydrazone (DAIH) to form fluorescent azine derivatives of the aldehydes, followed by HPLC separation of the derivatives and detection of the derivatives by fluorescence emission at

525 nm.[9]

This author's method and the Swarin method both depend on derivatization in ACN solution to minimize water interference and to facilitate direct analysis of the resulting derivative solutions. This direct analysis is attractive since sample preparation time is minimized and potential contamination by extracting solvents is eliminated.

Recently Swarin has reported testing the DNPH-ACN method for collection efficiencies.[10] He reports for gas phase trapping that the average efficiency for formaldehyde is 97.5% and for acrolein, butyraldehyde and benzaldehyde the collection efficiency averaged 95.0%. In contrast the aqueous DNPH methods had collection efficiencies that ranged from 9% for acrolein to 100% for benzaldehyde.

Other groups have tested for interferences in the DNPH analysis for aldehydes. Lowe showed that formaldehyde sampling with DNPH was not subject to interferences from ozone (up to 100 ppb) and sulfur dioxide (up to 90 ppb).[11] Grosjean has shown that the DNPH derivatives of the aldehydes are stable when exposed to air containing 150 ppb nitrogen dioxide, 200 ppb ozone and other common pollutants in urban air.[12] He has also shown that the trapping of formaldehyde, acetaldehyde and benzaldehyde is independent of the presence of other aldehydes.[13]

Another adaptation of the DNPH-ACN method was recently reported by Kuwata.[14] He used a DNPH-ACN solution to coat a C-18 based cartridge which was then used for atmospheric sampling. The cartridge is leached out after the air sampling with acetonitrile and the leachate analyzed.

In this report are discussed some of the details of the testing and use of the DNPH-ACN methods. Included are: the preparation of calibration standards (Chap. 2), HPLC column evaluation (Chap. 3), analytical testing (Chap. 4), dicarbonyl-DNPH analysis (Chap. 5), fluorescence methods (Chap. 6), preliminary cartridge testing (Chap. 8) and the results of atmospheric sampling in Schenectady, NY and Wilmington, NY (Chap. 7). The report concludes with some recommendations concerning the use of the DNPH-ACN methods and areas in which further research is required (Chap. 9).

Chapter 2

DNPH Derivatives

INTRODUCTION

Work began with the synthesis of authentic samples of the DNPH derivatives of a representative collection of aldehydes and ketones. The samples were to serve as calibration standards and to aid in the development of optimal HPLC conditions for analysis. In addition the samples could be supplied to other laboratories for calibration work.

EXPERIMENTAL

Synthesis of DNPH Derivatives:

The syntheses of the monocarbonyl DNPH derivatives were performed using standard techniques[15] with one exception. Instead of using ethanol as the solvent of choice for the reagent and for recrystallization, spectral grade methanol was substituted. It was found that the ethanol introduced acetaldehyde DNPH as an unwanted impurity in the derivatization process.

The crude DNPH derivatives were then recrystallized several times. Melting points were determined for comparison with literature values[16] and the purity of the samples were determined by HPLC. All the samples were in excess of 99% pure. The chief impurity in each case was a small amount of the unreacted DNPH reagent itself.

The preparation of the dicarbonyl DNPH derivatives is described in Chapter 5 of this report.

Calibration:

Solutions of the solid DNPH derivatives were prepared that ranged in concentration from about 4×10^{-4} M down to 1.2×10^{-6} M (for formaldehyde the high concentration was 8×10^{-4} M). If a 30 liter gas sample were collected in four milliliters of solution (the standard ambient sampling procedure) this would be equivalent to roughly a two thousand to six ppb gas phase concentration equivalent (formaldehyde would start at four thousand ppb).

The HPLC uv detector response was then determined for each of the solutions at two wavelengths, 254 nm and 360 nm.

RESULTS AND DISCUSSION

The melting points and HPLC purities are reported as part of Table 1.

We presently have on hand half gram quantities of the DNPH derivatives. The amount of sample required for an individual calibration is about ten milligrams, so we have sufficient material to supply samples to other laboratories. If this becomes an important task additional amounts of these derivatives can be made, or pure samples of other DNPH derivatives can be synthesized.

For all the derivatives for which calibration curves were determined the correlation coefficient was in excess of 0.999 over approximately two orders of magnitude in concentration. The ratio of the responses at the two wavelengths differed, and may prove useful for specific compound or compound class identification of unknowns. This is discussed further in dicarbonyl chapter. A response factor for each compound and wavelength was then determined from the linear least squares slope of the resulting graph.

Table 1. SOLID DNPH DERIVATIVES OF CARBONYL COMPOUNDS

Compound	MP (Lit) °C[2]	R.T.(min)*	% Purity
Formaldehyde	166 (167)	3.8	99.5
Acetaldehyde	157 (157)	4.8	99.7
Acrolein	158 (165)	5.5	99.1
Acetone	124 (128)	6.0	99.8
Propanal	149 (150)	6.5	99.8
2-Butanone	113 (115)	8.7	99.6
Glyoxal di-DNPH	312 (328)	9.6	99.6
Benzaldehyde	238 (237)	9.8	99.6
Cyclohexanone	159 (160)	12.2	99.4
Methylglyoxal di-DNPH	286 (299)	14.2	96.0
Biacetyl mono-DNPH	172 (?)	4.8	98.5
di-DNPH	320 (315)	24.8	95.0

*Alltech C-18 600 RPB Column, 25 cm x 4.6 mm, 10 microns, operated at 65% acetonitrile- 35% water, 1.5 ml/min.

Chapter 3

Column Evaluation[17]

INTRODUCTION

Accurate determination of individual aldehyde and ketone concentrations is dependent upon the extent to which the analytical conditions allow for the quantitative separation of the components of interest. In order to measure the effectiveness of analysis of a given column and separation conditions from a sample mixture, four parameters were evaluated:

Efficiency (N)=number of theoretical plates
Selectivity (alpha)
Capacity (k′)=partition ratio
Resolution (R)

The method of determination of each of these parameters can be found in reference 18.

The efficiency of a liquid chromatographic column is greatest for compounds with k′ values between 2 and 6. However, acceptable values are between 1 and 15. k′ essentially represents the time constraint of an analysis. That is, small k′ values indicate that components elute close to the unretained solvent while large k′ values improve separation but lead to long analysis times.[18]

Column selectivity, alpha, is a measure of the relative separation of two peaks. Values greater than 1.05 are generally accepted to provide 98% separation of peaks.[18]

The resolution may be improved by improving the efficiency, N. An efficient column keeps the bands from spreading and/or gives very narrow peaks. A well packed column of particle size 10 microns should be between 3500 and 10,000 theoretical plates.

Generally a resolution value, R, of 1.0 or greater is required for good quantitative or qualitative work.[18] With a 16:1 ratio of two components an R value of 1.0 provides a 99% valley minimum separation while an R value of 0.8 does not provide a minimum between the two components at the 16:1 ratio.

RESULTS

These parameters were used to compare two different

hpic columns, a Varian MCH-10 (C-18), 25 cm x 4.6 mm, 10 microns and an Alltech C-18 column, 25 cm x 4.6 mm, 10 micron (stock # 600 RPB, Alltech Associates, 2051 Waukegan Road, Deerfield, Ill. 60015), and then to determine the effect of solvent programming on the better of the two columns. In addition the Alltech column was evaluated for its ability to separate the C3 carbonyl compounds.

The results of these determinations are compiled in Table 2. From this table it is clear that conditions "c" (solvent programming) provided the best separations as indicated by the higher N, R, and k´ values. However, there are disadvantages to solvent programming which make its use impractical for present separations. While actual analysis time is comparable between conditions c and b (13.0 minutes for elution of the cyclohexanone hydrazone by solvent programming versus 12.5 minutes for isocratic) the programming requires that the column be brought back to initial conditions for the subsequent analysis. Total analysis time increases by three to five minutes per sample. Therefore, the use of column b run isocratically at 65% ACN gives separations which are most nearly within the ranges desired (as described above), yielding the necessary compromise between short analysis time and quantitative separation. The tables at the end of the chapter provide some summary chromatographic parameters for the Varian and Alltech columns for many of the DNPH derivatives synthesized in this work. The Table 3 below gives the important overall differences.

Table 3. Average Column Parameters

Parameter	Varian	Alltech
Efficiency (Theor. Plates)	3960	4610
Selectivity (Alpha)	1.24	1.33
Resolution[a] (R_S)	1.44	2.28
Analysis Time (mins.)[b]	9.5	12

[a] Biacetyl Di-DNPH not included
[b] For mono-DNPH derivatives

Experimentally, the improved separation obtained with the Alltech column allowed for the resolution of several pairs of components which were of identical molecular weight but different structures. Most notably, the

TABLE 2. Analysis Evaluation Parameters

2,4-DNPH deriv. of:	N a	N b	N c	α a	α b	α c	k' a	k' b	k' c	R a	R b	R c
2,4-DNPH	1869	2873	3100				1.03	0.81	1.24			
Formaldehyde	2241	4397	5615	1.41	1.99	2.15	1.44	1.62	2.67	1.84	5.43	7.07
Acetaldehyde	2284	4530	7015	1.17	1.38	1.34	1.69	2.23	3.59	1.05	3.43	4.06
Acetone	2454	5341	10607	1.20	1.39	1.29	2.03	3.11	4.65	1.26	4.03	4.60
Propanal	f	5454d	f	f	1.09d	f	f	4.4d	f	0.0	1.10d	f
MEK- syn	2228	5692	14884	f	f	f	2.56	4.53	6.01	f	f	f
- anti		5574	16273	1.0	1.08	1.05		4.90	6.33	0.0	1.13	1.35
Benzaldehyde	2145	5461	18943	1.14	1.16	1.09	2.92	5.68	6.90	1.09	2.22	2.38
Cyclohexanone	1963	5366	21319	1.09	1.28	1.13	3.17	7.27	7.81	0.71	3.87	3.62

a- Varian Micropak MCH-10 C18 reversed phase column; Isocratic 65% ACN

b- Alltech MCH-10 C18 reversed phase column; Isocratic 65% ACN

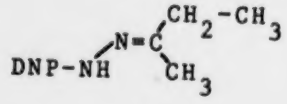
c- Alltech MCH-10 C18 reversed phase column; Solvent programming t=0 - 10 min, 55% - 75% ACN

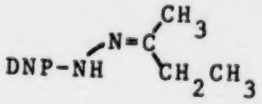
d- Data taken in a separate analysis

f- Data not available

separation of the acetone hydrazone from the propanal hydrazone (both C3 carbonyls) was effected with quantitative separation. Additionally two peaks were resolved from what had, on previous columns, been one 2-butanone hydrazone (methyl ethyl ketone) peak.

It is proposed that the 2-butanone hydrazone peaks result from the two stereoisomeric structures (below) of the hydrazone.





From steric considerations, it is predicted that the first conformation would be the more abundant as a result of decreased steric hindrance with the DNP unit. Analytically, the first conformation might be expected to elute last on a reversed phase column since the side chain which is more available for binding with the stationary phase is a C2 rather than a C1 as in the latter conformation. The reversed phase column separates according to side chain size with smaller side chains eluting first. The experimental results support these assumptions since the later of the two peaks is also the larger of the two.

One of the problems with the chromatographic work so far has been the inability to resolve the C_3 carbonyl compounds on the Varian MCH 10 (C-18) reversed phase HPLC column. Since the C_3 carbonyl compounds are likely to be important in laboratory studies and in ambient air work this was a serious deficiency. The column that appears to work best is the Alltech C-18 column.

In addition to the significant differences in resolution indicated above, the C_3 carbonyl compounds (acrolein, acetone and propanal) have retention times under the standard analytical conditions[7] of 5.5, 6.0 and 6.5 minutes respectively on the Alltech column. While baseline separation has not been achieved, it is possible to identify the individual compounds and, where the relative amounts of the materials are not too disparate, get analytical results. The higher resolution and C_3 separation has been achieved with only a minimal change in analysis time for the mono-DNPH materials (see Tables 4 and 5).

COMPOUND	R.T. (MIN)	PEAK WIDTH θ	COLMN EFFIC	COLMN CAPAC,K	SELECT.,ALPHA	RESOLUTION	R-S, RESOLN
DNPH	3.6	15	3168	0.64			
METHANAL	4.6	18.5	3488	1.09	1.71	20.04	2.99
ETHANAL	5.2	21.5	3217	1.36	1.25	10.35	1.50
BIACETYL	5.2	17	5146	1.36	1.00	0.00	0.00
ACETONE	6.2	24.5	3522	1.82	1.33	15.14	2.41
PROPANAL	6.2	24	3670	1.82	1.00	0.00	0.00
2-BUTANONE	7.5	28	3946	2.41	1.33	17.22	2.50
GLYOXAL*	8	30	3911	2.64	1.09	6.18	0.86
BENZALDEHYDE	8.7	33	3823	2.95	1.12	7.87	1.11
CYCLOHEXANONE	9.4	33.5	4330	3.27	1.11	7.75	1.05
METHYL GLYOXAL*	10.8	39	4218	3.91	1.19	13.31	1.93
BIACETYL*	15.3	50	5150	5.95	1.52	33.37	5.06

* = BI-DNPH

θ = 0.01 MINS

TABLE 4. Varian MCH-10 Column

COMPOUND	R. T. (MINS)	COLUM EFFIC.	COLUM CAP,K'	SELEC.,ALPHA	RESOLUTION	R-S, RESOLN.
DNPH	2.4	2395	0.85			
METHANAL	3.8	3995	1.92	2.27	11.64	5.47
DIACETYL	4.6	4827	2.54	1.32	5.52	2.57
ETHANAL	4.8	4769	2.69	1.06	1.44	0.60
ACROLEIN	5.5	4287	3.23	1.20	4.17	1.94
ACETONE	6	4958	3.62	1.12	2.93	1.26
PROPANAL	6.5	5423	4.00	1.11	2.83	1.23
2-BUTANONE	8.7	5668	5.69	1.42	9.52	4.60
GLYOXAL*	9.6	2503	6.38	1.12	2.35	1.25
BENZALDEHYDE	9.8	5605	6.54	1.02	0.76	0.26
CYCLOHEXANONE	12.2	5948	8.38	1.28	7.59	3.54
ME-GLYOXAL*	14.2	5020	9.92	1.18	4.99	2.38
DIACETYL*	24.8	5286	18.00	1.82	15.54	8.35

* = DI-DNPH

Table 5. Altech C-18 RPB 600 Column

Chapter 4

Analytical Testing

INTRODUCTION

In order to utilize any analytical method it is necessary to have some notion of the operational parameters of the method. Where possible intercomparisons should be made for analytical methods. In this regard the formaldehyde analysis was compared to a known standard method. It is also useful for field sampling to know how stable the reagent and the samples are. Work was performed to determine the stability of the DNPH reagent and to determine the stability of the sampled solutions. The detection limits of the method are useful for comparing methods and for evaluating the results from a particular method. A determination of the detection limits was performed according to a recommended procedure.[19]

EXPERIMENTAL

Formaldehyde Intercomparisons:

Cross comparison of the DNPH method and a standard method for formaldehyde was performed. The formaldehyde source was a permeation tube, using solid paraformaldehyde encased in a teflon tube held at a constant temperature. The rate of diffusion of the formaldehyde through the walls of the tube is a function of the temperature. A VICI Metronics Dynacalibrator Model 340 was used. The concentration of the formaldehyde in an air stream was varied by controlling the temperature and the rate of flow of the diluent gas. By using two temperatures, 85° and 90° C, and flow rates for the diluent air stream from 1 to 20 liters/minute, we were able to generate formaldehyde-air mixtures in the concentration range 60 to 1400 ppb. The diluent air stream was Linde hydrocarbon free air.

The air stream was sampled in the standard fashion, first by the DNPH technique and then by sampling into a chromotropic acid solution (CA).[20] In general the sampling times required in the CA samples were twice as long as for the DNPH samples for the lower concentration work.

Calibration of the Chromotropic Acid Assay:[21]

Stock formaldehyde solutions were prepared from 96% paraformaldehyde. A stock concentration of 6.1X10-2 molarity was obtained by diluting 0.1919 grams of paraformaldehyde with 10% sulfuric acid in a 100 ml

volumetric flask. With the aid of a magnetic stirrer, the paraformaldehyde took approximately 24 hours to go into solution. Standard solutions of varying concentrations were obtained by simply diluting the stock solution. The formaldehyde solutions are stable for only one or two days.

The standard reaction products were obtained by combining 5.0 ml of the chromotropic acid reagent with 1.0 ml of a formaldehyde stock solution in a 10.0 ml volumetric flask. The solution was then brought to volume with concentrated sulfuric acid.

The absorbance of each standard mixture was then measured at 580 nm. A calibration curve was constructed by plotting absorbance versus concentration.

Impinger Technique:[21]

Both the chromotropic acid and the DNPH techniques employ the same sampling apparatus. That is, two impingers, a pump, and a flowmeter connected in series.

The second impinger is used to check sampling efficiency by determining the amount of aldehyde getting past the first impinger.

For the chromotropic acid technique 10.0 ml of sampling reagent was added to each impinger. After sampling, the absorbance of the colored reaction product was measured at 580 nm. The concentration was then obtained from the calibration curve.

DNPH Reagent Stability Tests:

Four DNPH reagent solutions were prepared and stored in different types of containers. One solution had no acid added. The solutions are listed below.

1. Plastic (bakelite) capped vial.
2. Ground glass container
3. TEFLON capped vial
4. TEFLON capped vial (no acid added to the DNPH-acetonitrile solution)

Periodically samples from each of the solutions were withdrawn and analyzed by HPLC.

Analysis Solution Stability:

The stability of the solutions after atmospheric sampling was determined. Samples of the Schenectady, N.Y. air were taken by passing 90 liters of air through the DNPH-acetonitrile solutions in the standard fashion. The resulting solutions, stored in teflon capped vials in a refrigerator (at $0^{\circ}C$) , were periodically analyzed over several weeks.

Limit Of Detection:[21]

Limits of detection (LOD) for the DNPH-acetonitrile technique were determined according to a procedure recommended by G. Long and J. Winefordner.[19] The method involved analyzing a series of reagent blanks from which data the background levels of aldehydes were calculated based on a 90 liter air sample diluted to 4.0 ml. The standard deviation for each aldehyde detected was then calculated. The limit of detection was defined as a signal which was greater than three standard deviations from the average background signal. The limit of quantitation was defined as a signal greater than ten standard deviations from the average background signal.

RESULTS

Formaldehyde Intercomparisons:

Table 6 lists the results for the formaldehyde intercomparison work and a plot of the results is given in an attached Figure 1.

Table 6. DNPH-CA Intercomparison

CA (ppm)	DNPH (ppm)
1.30	1.40
0.81	0.71
0.45	0.51
0.19	0.23
0.14	0.14
0.10	0.11
0.099	0.11
0.061	0.058
0.060	0.072

In the figure the line drawn has a slope of 1.00 and would be the expected line if the results for the two techniques had given the same values. The actual least squares slope is 1.02 with a correlation coefficient of 0.993. A weighted least squares analysis gives a percent error for the measurement of 10.2%. Within about ten percent the two results are in agreement. The variation is probably due to the method of sampling, namely sampling sequentially and, in some cases, for different amounts of time.

DNPH Reagent Stability Tests:

After two weeks there was no detectable contamination in solutions 2-4. In the plastic capped vial, however, there was a noticeable build-up of a peak having the same retention time as the benzaldehyde DNPH derivative. The amounts were substantial enough (180 ppb-30 liter

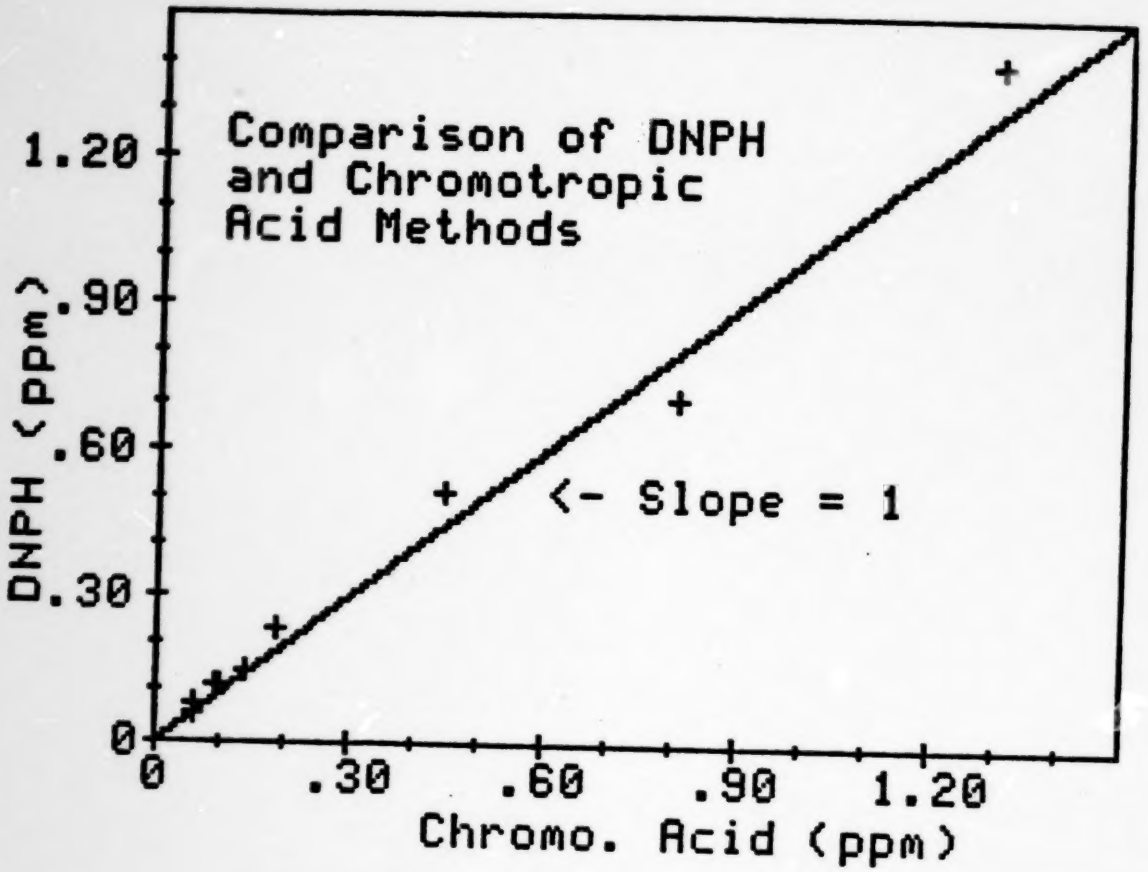


Figure 1. Comparison of DNPH and Chromotropic Acid Methods for Formaldehyde Determination

equivalent) to preclude using the solution for sampling. The remaining three solutions were periodically monitored for the build up of contaminants. In addition acid was added to a portion of the fourth solution after 166 days. The results of the work are displayed in Figure 2. A steady build-up of impurities is observed in the reagent regardless of the container if acid has been added. In the unacidified reagent there is no increase in contamination until acid is added. The results imply that as a matter of procedure one can either make up fresh reagent with acid and use it within two weeks or make up an acetonitrile solution of the DNPH and then add acid just prior to use. The latter procedure has been adopted in this laboratory.

A substantial fraction of the contaminant is a material with a retention time shorter than the DNPH. There are several possibilities for the identity of the contaminant. Nucleophilic addition of the DNPH to either the acetonitrile solvent (to give a compound analoguous to an amide) or to dissolved carbon dioxide (to give a compound analogous to a carbamate) might account for the build-up of the impurity with time. The products of the above reactions would be relatively stable and effectively would tie up the DNPH. Since over a period of time the DNPH concentration would be reduced, an old reagent would be less effective at trapping atmospheric carbonyl compounds.

Analysis Solution Stability:

The results for the analysis of the stored DNPH-acetonitrile sampled solutions is listed below. Within the accuracy of the individual analyses, the sample appears to be stable for as long as three weeks after sampling.

Table 7. Analysis of Aged DNPH-sampling solutions

TIME (weeks)	FORMALDEHYDE (ppb)
initial	5.1
1	5.8
2	4.5
3	4.9

Limit of Detection:[21]

According to the method prescribed in the experimental, detection limits for a 90 liter sample were found to be as follows:

Figure 2. Build-up of Impurities in Stored DNPH Solutions

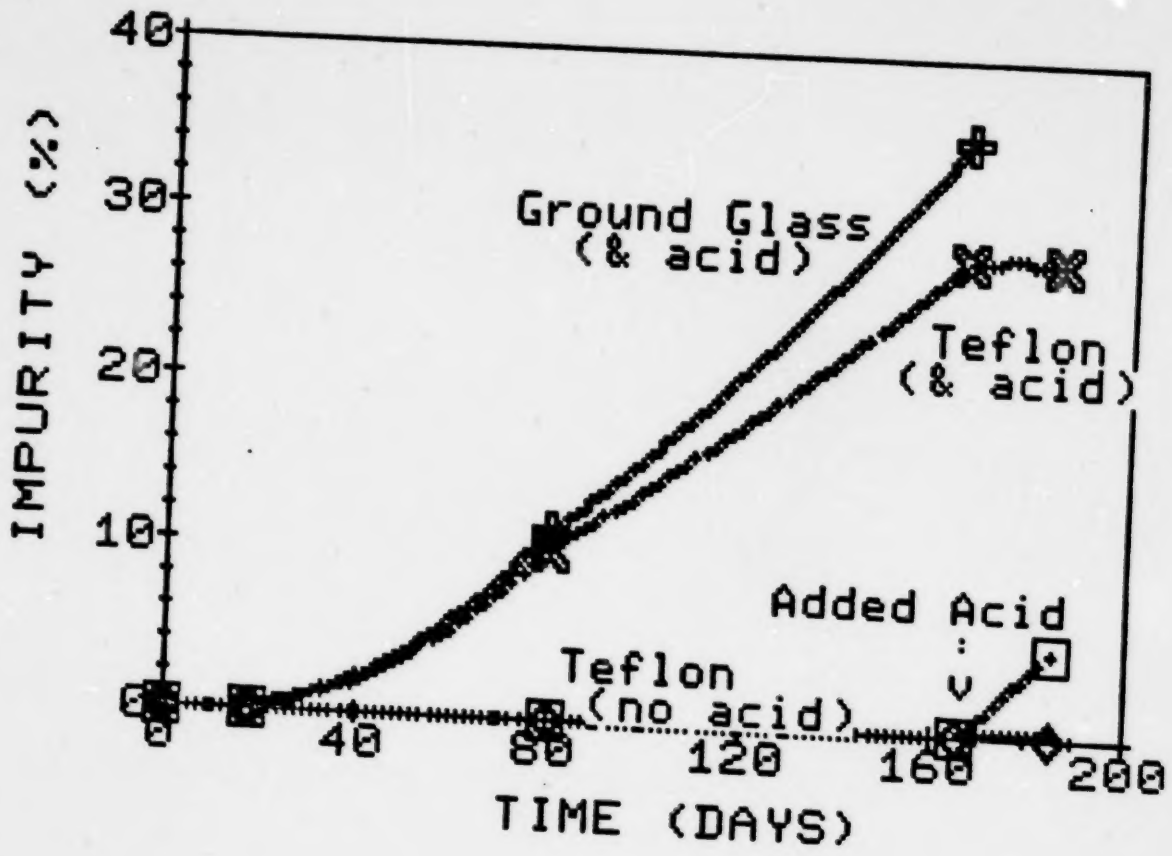


Table 8. Limits of Detection for DNPH-ACN Method

	Det. Limit(ppb)	Quant. Limit(ppb)
Form.	0.10	0.32
Acetald.	0.16	0.53

The formaldehyde detection limit can also be expressed as 2.8 ng/ml of formaldehyde in the analyzed solution and for acetaldehyde the corresponding number is 6.6 ng/ml. In addition since the amount of solution actually injected into the HPLC is 10 microliters the absolute limits of formaldehyde and acetaldehyde detected are 28 and 66 picograms respectively. With the exception of acetone, the other aldehydes and ketones gave about the same instability in baseline as the acetaldehyde and their detection limits are therefore about the same (0.16 ppb LOD and 0.53 ppb LOQ for a 90 l sample). Acetone was found in the reagent at exceedingly high and unstable concentrations. The contamination of the reagent, apparently due to the impurity in the acetonitrile, led to the inability to monitor acetone levels.

Chapter 5

Dicarbonyl Compounds

INTRODUCTION

One of the potential applications of the various aldehyde-ketone analysis techniques is to the analysis of dicarbonyl compounds. In particular, the C2 (glyoxal), C3 (methylglyoxal, pyruvaldehyde) and C4 (biacetyl, 2,3-butanedione) compounds represent the most interesting of the dicarbonyl compounds. Previous work had shown that DNPH (2,4-dinitrophenyl hydrazine) derivatives could be formed and detected under the conditions of the analysis, but there was ambiguity about the nature of the material being detected in the analysis (mono or di-DNPH derivative) and whether there was some analytical interaction among the above dicarbonyl compounds.[22] In the literature the di-DNPH derivatives of dicarbonyl compounds are known as 2,4-dinitrophenyl osazones.

In order to resolve the ambiguities efforts were made to determine the chromatographic behavior of the mono and di-DNPH derivatives of the C2-C4 dicarbonyl compounds. Two approaches were used. In the first approach solutions were made with large and small dicarbonyl/DNPH ratios. In the second approach attempts were made to isolate authentic solid samples of the mono and di-DNPH derivatives.

EXPERIMENTAL

Varying Dicarbonyl/DNPH Ratios:

By varying the ratio of dicarbonyl compound to DNPH reagent it should be possible to form the mono-DNPH derivative at high ratios (> 90), excess carbonyl compound, and the di-DNPH at low ratios (< 0.01), excess DNPH reagent. The solutions of appropriate ratio were made up in acetonitrile with the low concentration component between 1-6 x 10^{-5} M. Biacetyl was available as a pure (distilled) compound; glyoxal and methylglyoxal were used as 40% aqueous solutions. After mixing in the appropriate ratios, the solutions were warmed at 50° C for 30 minutes. The solutions were then analyzed by direct injection, under the standard analytical conditions,[7] into the HPLC. The results are presented in Table 9 below. The retention times listed are those using a Varian 25 cm RP C-18 column.

Table 9. ANALYSIS OF DICARBONYL-DNPH REAGENT SOLUTIONS

Compound	Dicarb/DNPH Ratio	R.T. (mins.)
Glyoxal	130	4.0
	0.01	7.9
Methylglyoxal	110	4.2 (20%), 4.5 (80%)
	0.01	10.7
Biacetyl	92	5.0
	0.007	15.1

Synthesis of DNPH Derivatives:

The second approach to establishing the identity of the dicarbonyl analytical materials involved the preparation of authentic solid samples. The approach to the synthesis was the same as that in the above experiments. Reaction with excess dicarbonyl compound was expected to produce the mono-DNPH derivatives and reaction with excess DNPH was expected to produce the di-DNPH derivatives. For practical reasons, the excess reagent could be used in no higher concentration than about 10 to 1. In the attempted preparation of the mono derivatives the DNPH solution was added to a solution of excess dicarbonyl compound. The reactions were performed in methanol and the products recrystallized from methanol

The preparation of the solid di-DNPH derivatives was done by adding a solution of the dicarbonyl compounds in methanol to an excess of the DNPH in methanol and then refluxing for thirty minutes before cooling and isolating the product. The pure liquid was used as starting material for the biacetyl preparation and a 40% aqueous solution was used for the methylglyoxal reaction. The solid glyoxal trimeric dihydrate (Sigma Organic Chemicals) was used as starting material for the glyoxal di-DNPH preparation. The products of each of the reactions was recrystallized from methanol.

RESULTS AND DISCUSSION

The experiments at high dicarbonyl compound to DNPH ratios show short retention time peaks (4-5 minutes), as expected for polar C2-C4 mono-DNPH materials. In comparison the retention time for acetone-DNPH is 6.2 minutes under the same conditions. There are two peaks observed in the high (110) ratio run for methylglyoxal, one at 4.2 mins. and the other at 4.5 mins, comprising 20% and 80% of the mixture respectively. Since there are two possible mono-DNPH's of methylglyoxal,

(A) $CH_3C(=NNHDNP)CHO$, (B) $CH_3COCH(=NNHDNP)$

where A represents derivatization at C_2 and B represents derivatization at C_1, the two peaks presumable represent the two isomers. It is likely that the larger component is the aldehyde derivative B, since there is less steric hindrance to destabilize it. Also the longer retention time is consistent with the behavior of the reversed phase column which tends to bind more strongly to longer contiguous chains.

In contrast the experiments at low ratios, where di-derivatization is likely, show longer retention time materials (7.9-15.1 minutes). These longer retention time materials are, presumably, the di-DNPH derivatives. The low ratio conditions, excess DNPH, are the conditions that pertain to the standard analytical runs.

The preparation of the mono-DNPH derivatives was successful only for biacetyl. The solids isolated from the reaction of excess dicarbonyl compound, in the case of glyoxal and methylglyoxal, showed significant contamination with the di-DNPH derivative (about 50%). Apparently the mono-DNPH derivatives, for those two dicarbonyl compounds, are sufficiently soluble in the methanol reaction solvent so that they can react with a second molecule of the DNPH reagent. Recrystallization of the materials produced no significant increase in purity. The biacetyl did give a product that was, by HPLC, essentially pure (98.5%) and had the same retention time as material earlier (above) identified as the mono-DNPH derivative.

HPLC analysis showed that the materials were reasonably pure (>95%) and that the contaminants were small amounts of DNPH and the mono-DNPH derivatives. The purity and retention time data for the isolated solid derivatives are given in in Chapter 2.

The solid derivatives were used to make up a solution to calibrate the HPLC responses. Also estimates of the HPLC responses for the mono-DNPH derivatives of glyoxal and methylglyoxal were calculated from the dicarbonyl/DNPH ratio experiments described before. The results of the calibration work and the estimates are given in Table 10.

There are some apparent correlations in the response factors of the various DNPH derivatives by functional group class. The most sensitive measure of the functional group class appears to be the 360 nm/254 nm uv response ratio. This ratio may be useful for the positive identification of a compound in conjunction with its retention time or may prove useful when dealing with materials of unknown retention time in classifying them

Table 10. HPLC DATA FOR THE DICARBONYL-DNPH DERIVATIVES

Compound	UV Det. (nm)	R. T. (min)	Response ($\times 10^7$)[1]	360/254
Glyoxal				
Mono-DNPH	254	4.0	5.20[2]	0.35
	360		1.80[2]	
Di-DNPH	254	7.9	3.34	0.97
	360		3.23	
Methylglyoxal				
Mono-DNPH	254	4.2, 4.5	4.20[2]	0.43
	360		1.80[2]	
Di-DNPH	254	10.7	2.78	0.99
	360		2.75	
Biacetyl				
Mono-DNPH	254	5.0	3.33	0.32
	360		1.05	
Di-DNPH	254	15.1	2.29	1.03
	360		2.35	

1. Units of Molarity/mm^2 for 0.08 absorbance and 10 mm/min chart speed. The analysis was performed on a Varian 25 cm x 4.6 mm RP C-18, 10 micron column..

2. Estimated from the addition of known quantities of DNPH to solutions of excess dicarbonyl compound.

as to a functional group type. The large ratio (1.0) given by the dicarbonyl di-DNPH derivatives is very easily distinguished from the corresponding ratio for simple monocarbonyl DNPH derivatives (0.49) and should make it relatively easy, in a given analysis, to positively identify the dicarbonyl components even when they don't possess unique retention times. The short Table 11 below summarizes this work.

Table 11. DNPH UV RESPONSE RATIO BY COMPOUND CLASS

Compound Class	360 nm/254 nm Response
Monocarbonyl DNPH	0.49 ± 0.03
Dicarbonyl Mono-DNPH	0.37 ± 0.05
Dicarbonyl Di-DNPH	1.00 ± 0.03

It was apparent in the work with the solid di-DNPH derivatives that they had only very limited solubilities in the acetonitrile. For the biacetyl di-DNPH the maximum solubility appeared to be about 10^{-3} M at room temperature in pure acetonitrile. The other di-DNPH derivatives appeared to have similar solubility limits. In performing atmospheric sampling into four milliliters of DNPH reagent this would correspond to 32 ppb in a 30 liter gas sample (1 ppm in a 1 liter gas sample) as the maximum concentration that would produce a homogeneous analysis solution. This of course ignores the effect on the solubility of the derivative of the presence of excess DNPH and any other of the dicarbonyl di-DNPH derivatives. The system would be a multicomponent one with a complex phase diagram for solubility but under the more complex conditions it would undoubtedly be the case that the solubility would be decreased over the solubility in pure acetonitrile.

It was also observed that when saturated solutions of the biacetyl di-DNPH derivative were injected into the HPLC the resultant peak tailed significantly. This was probably due to the precipitation of the derivative on the HPLC column. The eluting solvent for analysis is a 65% acetonitrile/35% water mixture. The di-DNPH derivative is virtually insoluble in water. The observed peak, in the HPLC, corresponded to a saturated solution in the eluting solvent, and the tailing would be the precipitated material being leached off the column by the continuing flow of the eluting solvent.

In reviewing the Kamens' work on the dicarbonyl compounds, it was apparent from their chromatograms (see Figure 8 in reference 22) that they were working with saturated solutions.[22] Each of the chromatograms shows significant tailing of the di-DNPH derivative peaks both within a given run and from run to run. The latter implies that there was still precipitated material on their columns from previous injections. This may be the cause of the odd analytical interactions observed. At the saturation limits for these di-DNPH derivatives it is apparent the analysis will be faulty. It is tentatively recommended that if the method is to be used for dicarbonyl compounds that the solutions prepared be kept at least a factor of 10 (and better a factor of 100) below the solution saturation levels of the di-DNPH derivatives in acetonitrile.

Chapter 6

Fluorescence Methods

INTRODUCTION

A large number of hydrazine and hydrazone derivatives have been used for the determination of aldehydes. In this chapter, largely quoted from the senior thesis of Carol Berman[23], the use of 2-diphenylacetyl-1,3-indandione-1-hydrazone (DAIH), and 1-dimethylaminonaphthalene-5-sulfonylhydrazine (dansyl hydrazine) as analytical reagents for aldehyde determination is described. Both reagents employ fluorescent chromophores, and should be detectable at extremely low concentrations.

DAIH was first introduced as a useful reagent for characterizing aldehydes in 1958 by Braun and Mosher.[24] It forms fluorescent derivatives with aldehydes in less than 10 minutes by the standard acid catalyzed hydrazine reaction with carbonyl compounds.

In 1981 Swarin presented an improved method[9,10,25] whereby sample collection and derivatization was performed directly in midgit impingers containing the solvent (acetonitrile), the derivatizing agent (DAIH), the reactant aldehydes, and the catalyst (HCl). This eliminates time consuming recovery steps and allows for direct injection of the sample into the chromatograph. Reverse phase HPLC with fluorescence detection was used to separate and quantitate the aldehydes.

The 1-dimethylaminonaphthlene-5-sulfonyl (dansyl) group has been proven a useful fluorophore in qualitative and quantitative analysis of many compounds. Dansyl chloride was first introduced by Weber[26] in 1952 in his work on protein structure. It was reintroduced by Gray and Hartley[27] for peptide and amino acid analysis and used by Seiler and Weichman[28] for amines in general.

In 1970, Seiler and Weichman[29], and Graef[30], and in 1971, Chayen[31] each separately suggested that substitution of the chlorine atom on dansyl chloride by the hydrazine group would convert the molecule into a good reagent for analysis of carbonyl compounds. Since then it has been used extensively in biological and biochemical studies. Most commonly it has been used in the analysis of reducing sugars[32], ketosteroids[33], oxosteroids[34], bile and ribonucleic acids[35,36], and carbohydrates.[37]

In this chapter is described the condensation of simple aldehydes with dansyl hydrazine and then the method is considered for adaptation to ambient air measurements.

EXPERIMENTAL

Apparatus used

A Varian Cary Model 118 Spectrophotometer was used for UV/Visible absorption spectroscopic work. A Perkin-Elmer Hitachi MPF-2A Fluorescence Spectrometer with a Hitachi Recorder QPD 33 and a Perkin Elmer 150 Xenon Power Supply was used for fluorescence spectroscopic work. A Varian 5000 HPLC with built-in 254 nm detector and a Tracor 970A variable wavelength detector was used for the uv-HPLC work. The other detector was the Kratos-Schoeffel Model FS 950 Fluoromat fluorescence detector.

Reagents Used

The DAIH, dansyl chloride, and all aldehydes were obtained from Aldrich Chemical Company. All were used as received except for acetaldehyde and propionaldehyde which were distilled before use. Dansyl hydrazine was obtained from Pierce Chemical Company and used without further purification. All other chemicals used were the best available from various suppliers.

Preparation and Identification of Aldehyde Derivatives of DAIH

A few milligrams of the azine derivatives of formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, benzaldehyde, cyclohexanone, and valeraldehyde were prepared according to the procedure of Braun and Mosher.[24] All quantities were scaled down by a factor of one-eighth. A mixture of 0.198g (5.63×10^{-4} moles) of DAIH, 6.25×10^{-4} moles of carbonyl compound, 3 ml of $CHCl_3$, and 50 microliters of concentrated HCl was warmed at reflux until a deeply colored nearly clear solution was obtained. Reaction time was always less than 10 minutes. The solution was then filtered hot by gravity to remove any unreacted reagent. Three ml of methanol was added to the filtrate to induce crystallization. If there was no immediate crystallization, as was the case for formaldehyde, acrolein, propionaldehyde, and valeraldehyde, the solution was evaporated until crystals came out of solution. The crystalline product was then filtered and recrystallized once from a 1:5 $CHCl_3$:CH_3OH solution (30 to 60 ml depending on the azine). Derivatives were brightly colored, fluorescent, crystalline solids.

The reactants were always added in the order listed above. The order seemed to be unimportant for the

preparation of the derivatives except in the case of formaldehyde. An oily residue was left after both crystallization and recrystallization. However when the order was altered and the formaldehyde was added last, crystals were formed. Formaldehyde is quite reactive and if it is added to the reaction mixture prior to the catalyst it may begin to polymerize because it cannot yet react with the derivatizing agent.

The identity of these derivatives was confirmed by comparing melting points and retention times of the derivatives to those reported by Braun and Mosher[24] and Swarin.[9,10,25] (See Table 12.) A few crystals were dissolved in acetonitrile and reverse phase HPLC with UV detection at 254 nm. and 425 nm. was used for this qualitative analysis. The following program was used: flow rate = 1.0 ml/min., 76% acetonitrile/24% water for 18 min., increasing acetonitrile to 100% over the next 12 min., and continuing at 100% acetonitrile for 8 more minutes. Refer to Figure 3.

Table 12. IDENTIFICATION OF AZINES

AZINE OF	EXPER MP (C)	LIT MP[24] (C)	EXP RT (MIN)	LIT RT[25] (MIN)
formaldehyde	152-158	169-170	10.3	10.0
acetaldehyde	181-182	179-180	12.4	11.3
acetone	226-227	222-223	13.4	13.0
acrolein	-------	86 -87	13.1	14.6
propionaldehyde	137-138	133-135	13.8	15.6
benzaldehyde	239-240	242-243	25.5	25.0
cyclohexanone	248-249	241-244	----	----
valeraldehyde	154-156	159-161	25.2	28.0
reagent	-------	-------	5.0	5.0

Slight differences in melting points may be attributable to experimental uncertainties, whereas differences in retention times were due to slightly different chromatographic columns.

Characterization of Azines by Ultraviolet, Visible and Fluorescence Spectroscopy

Preliminary UV/Vis absorption spectra of the reagent and the derivatives of acetaldehyde, acetone, benzaldehyde and valeraldehyde were prepared. The shapes of the curves were very similar. Acetone and acetaldehyde were then chosen as a characteristic ketone and aldehyde to study in more detail. Formaldehyde was going to be used because of its importance in pollution studies, however due to the problems with its preparation, acetaldehyde was substituted. Solutions of the two azines were prepared in acetonitrile solution.

Acetone Azine: A visible absorption spectrum (600-350 nm.) was run using the following conditions:

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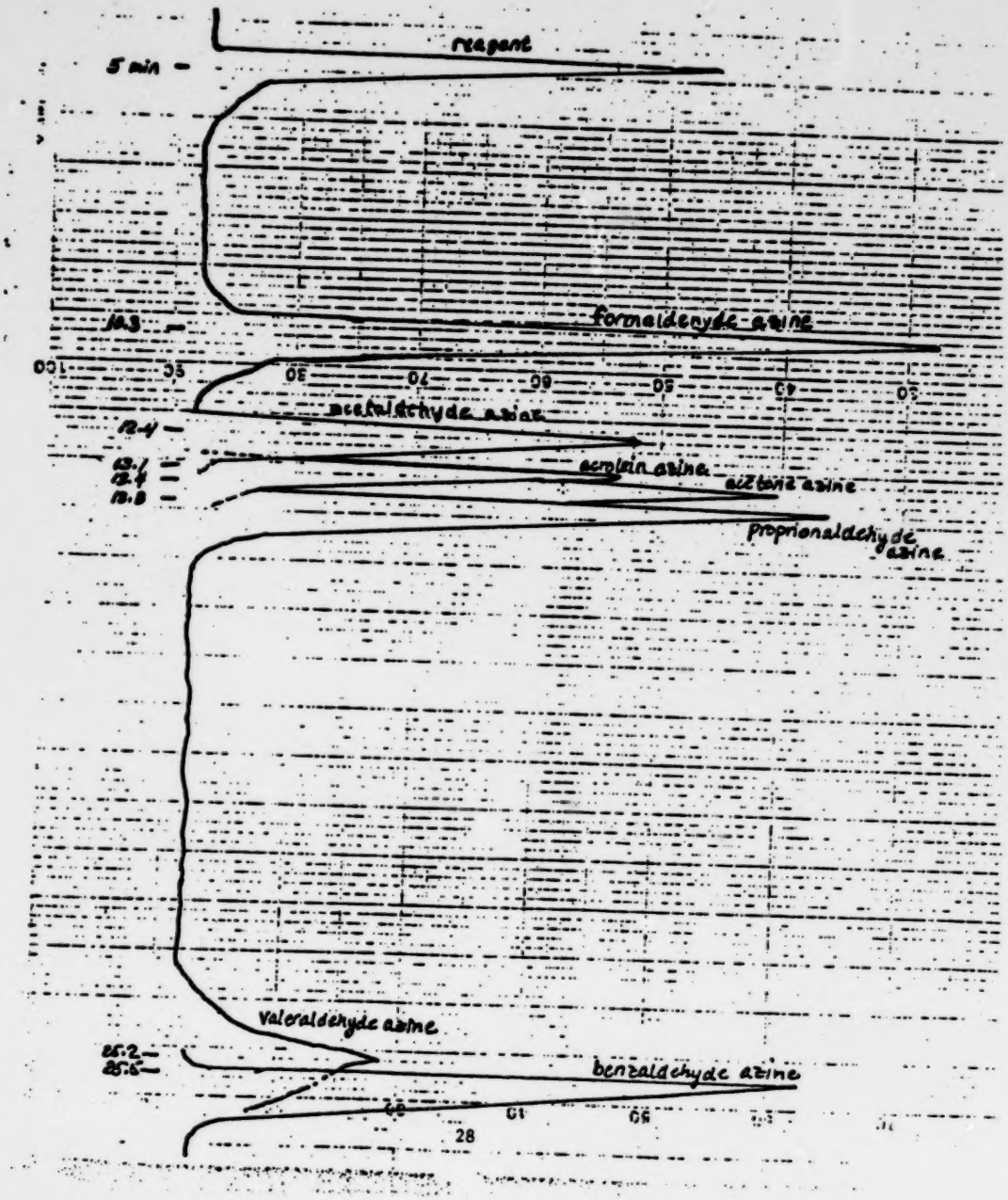


FIGURE 3. HPLC Separation of Seven DAIH-Aldehyde Azines

absorbance = 2, scanspeed = 2.0, autoslit, gain = 30, and 20 nm./in. The concentration of the solution was 1.27 x 10 -4 M, Wavelength of maximum absorbance was found to be 410 nm. (see Figure 4). A UV spectrum was next run (350-200 nm.) with the same conditions as above (see Figure 4). The compound showed intense absorption throughout the entire UV range. It is worth noting that the minimum absorbance on the UV spectrum, occurring at 250 nm., is greater than the maximum absorbance in the visible spectrum, occurring at 410 nm. Fluorescence emission spectra were next obtained using slits = 8 (excitation) and 4 (emission) with an excitation wavelength of 410 nm. and then 290 nm., the maximum absorbance wavelengths from the absorption spectra. In both cases, the maximum fluorescence intensity was found to be at 525 nm. (see Figure 5). With the excitation wavelength at 410 nm., however, a more intense peak resulted than when using 290 nm. Finally, a fluorescence excitation spectrum was obtained using slits as above and an emission wavelength of 525 nm. This spectrum had 2 peaks, maximum occurring at 330 nm. and 410 nm.

Acetaldehyde Azine: Identical runs were made replacing the acetone azine solution with a 1.00 x 10 -4 M solution of acetaldehyde azine in acetonitrile and the same results were obtained. The wavelengths of maximum absorbance were 410 nm. and 290 nm., respectively, the azine absorbing more intensely in the UV range (see Figure 4). Maximum fluorescence intensity for emission spectra using excitation wavelengths of 410 nm. and 290 nm. was found to be 525 nm. again, and as before, when using 410 nm. to excite, a better spectrum was obtained (see Figure 5). The excitation spectra were also quite similar.

At this point, it was presumed that all of the azines would have comparable spectroscopic properties.

Fluorescence Detection of the Azines After Chromatographic Separation

The fluorescence detector was installed on the HPLC. From the above investigation an appropriate source and appropriate filters were chosen to obtain optimum detection. The FSA 115 excitation lamp was chosen, which emits at 405-480 nm. The FSA 403 excitation filter was chosen, which has a 365 nm. cutoff. The FSA 430 emission filter was chosen, which has a 500 nm. cutoff.

A chromatogram for a 1.27 x 10 -4 M solution of acetone azine in acetonitrile was obtained with fluorescence detection as described and UV detection at 254 nm. For maximum on scale response, a sensitivity of RANGE = 5 on the fluoromat and attenuation = .08 on the UV detector was needed. Measurements approximately 50

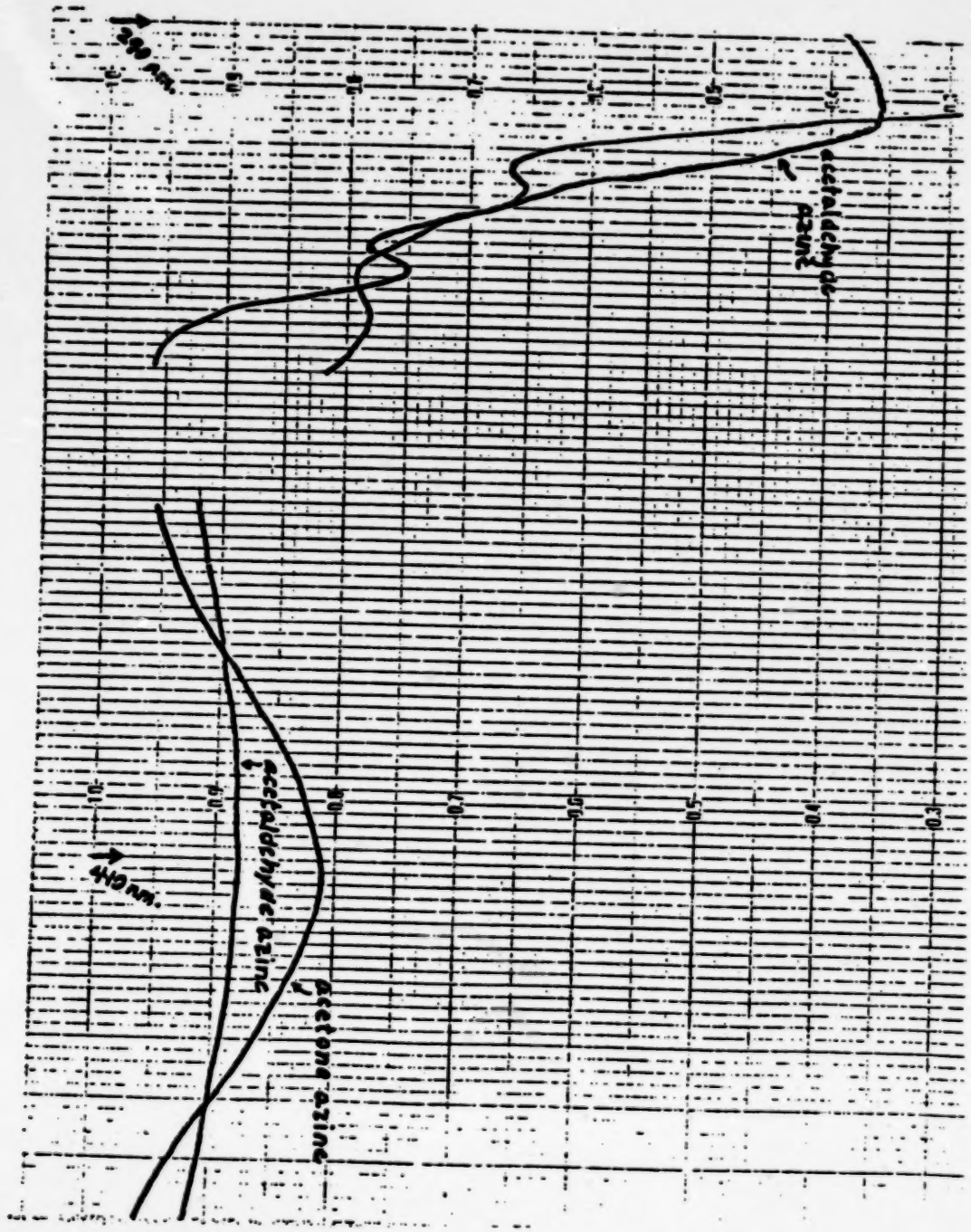


Figure 4. UV/VIS Absorption Spectra of Acetone and Acetaldehyde Azine

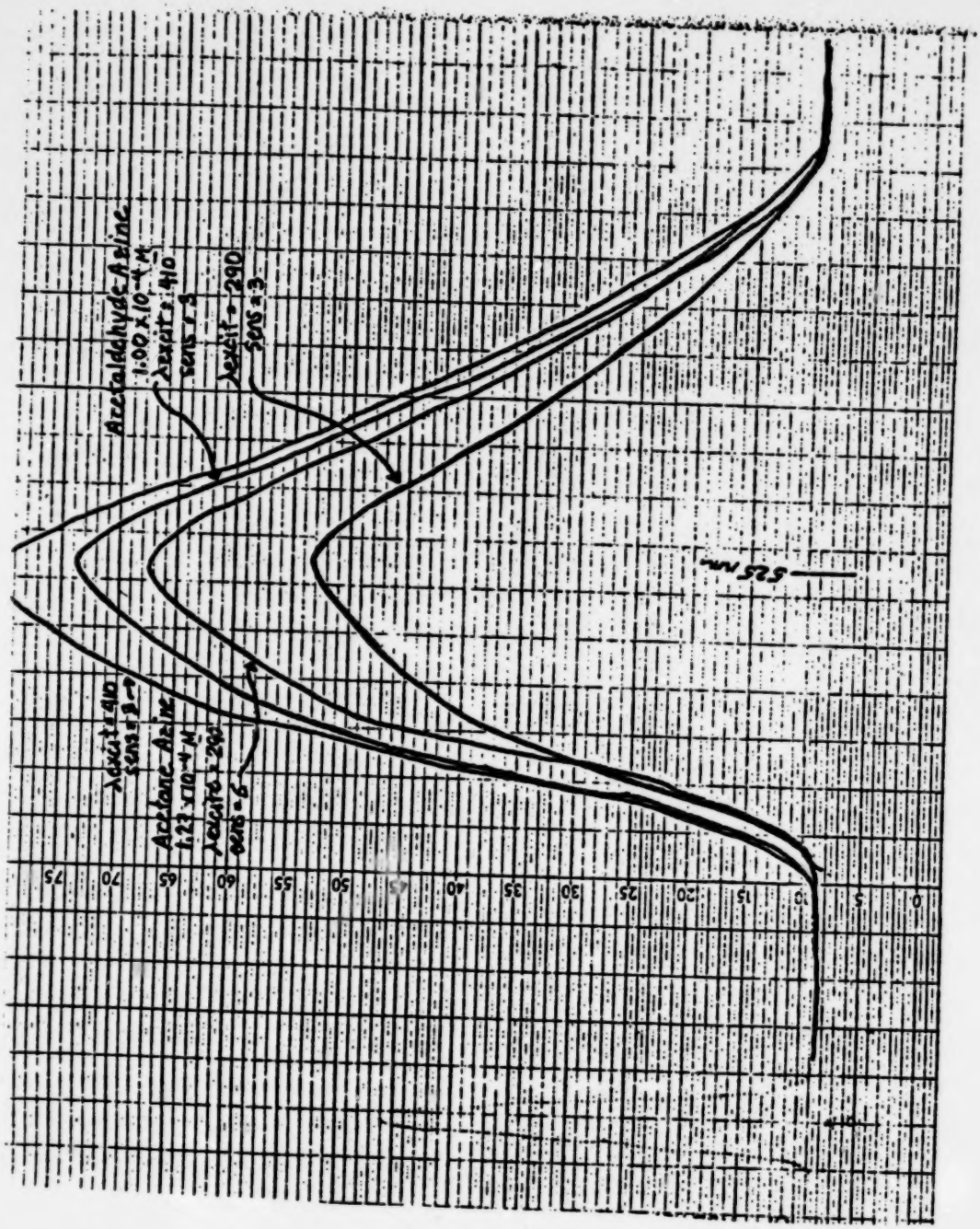


FIGURE 5. Fluorescence Emission Spectra of Acetone and Acetaldehyde Azines

times more sensitive may be made with fluorescence detection and approximately 40 times more sensitive with UV detection judging by the available attenuation settings.

Then a chromatogram for a 1.00 x 10 -3 M solution of acetaldehyde azine in acetonitrile was obtained. For the highest on scale response a sensitivity of RANGE = 1 on the fluoromat and attenuation = .16 on the UV detector was needed. Measurements approximately 100 times more sensitive may be made by fluorescence detection and approximately 80 more sensitive by UV detection.

A preliminary interpretation would suggest that for the DAIH derivative, the fluorescence emission at 525 nm. with excitation at 425 nm. (which was determined to be the optimal conditions for maximum fluorescence intensity) is not significantly more sensitive than absorption at 254 nm., which is not even the maximum absorbance in the UV range.

Calibration curves were then prepared for acetone and acetaldehyde azine determination using the fluorescence method and ultraviolet absorption analysis at 254 nm. and at 290 nm. in order to calculate detection limits (290 nm. was chosen since it is the wavelength of maximum absorbance for the derivatives.) See Figures 6 to 11. The graphical method described by Long and Winefordner[19] was used where $C = kS/m$: C is the lowest detectable concentration with the given instrument, k is the number of standard deviations away from the blank that is a significant result (=3), m is the slope of the calibration curve and S is the standard deviation of blank readings when the number of blank readings was 20. These concentrations were then converted to parts per billion using appropriate conversion factors. Unfortunately, detection limits could only be calculated for ultraviolet absorption data because of problems that later arose with the fluorescence detector; baselines were too noisy to get accurate readings.

The detection limit for ultraviolet absorption at 290 nm. was found to be 0.34 ppb for acetone azine and 0.1 ppb for the acetaldehyde azine. A value of 4.5 ppb for the acetaldehyde azine detection limit for the fluorescence method was published by Swarin.[9,10,25] The value is substantially larger than the values obtained for ultraviolet absorption detection of the azine. Detection limits for the DNPH method were calculated (see Chapter 4) by Peter Schulam.[38] He found a detection limit of 0.16 ppb for detection of aldehydes other than formaldehyde.

Figure 6. Acetone Azine Fluorescence Response Calibration

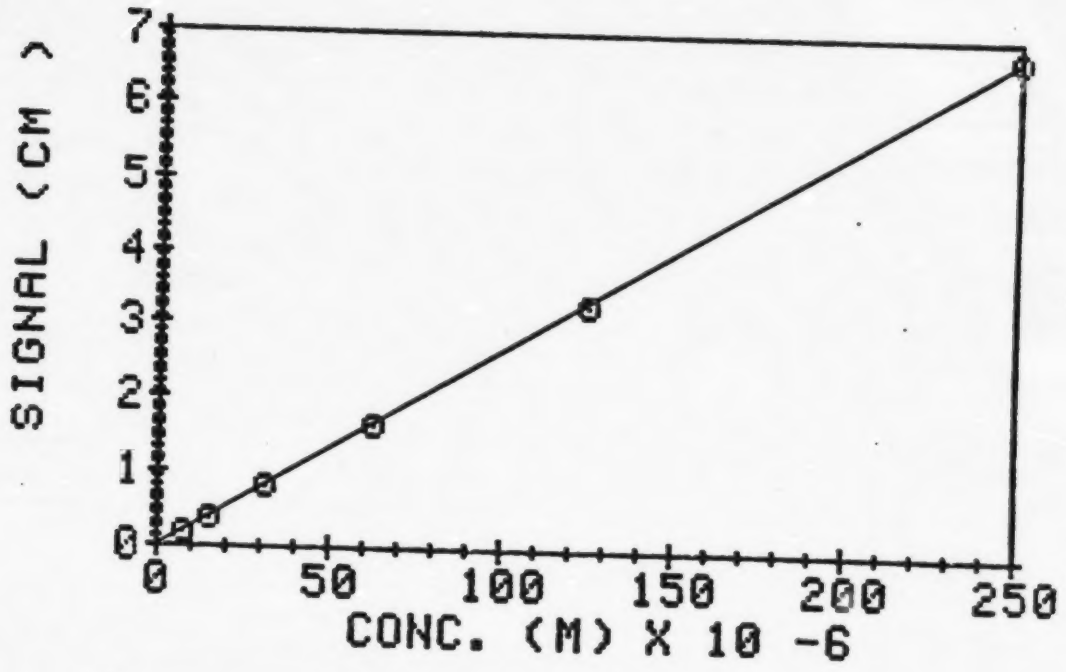


Figure 7. Acetone Azine 254 nm UV Response Calibration

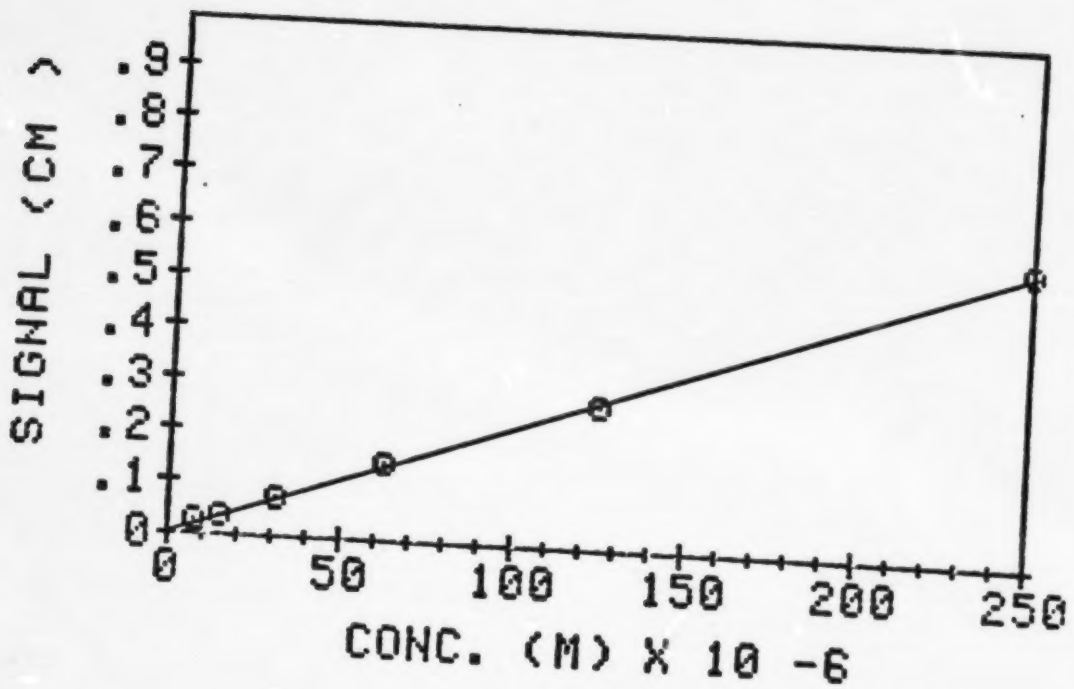
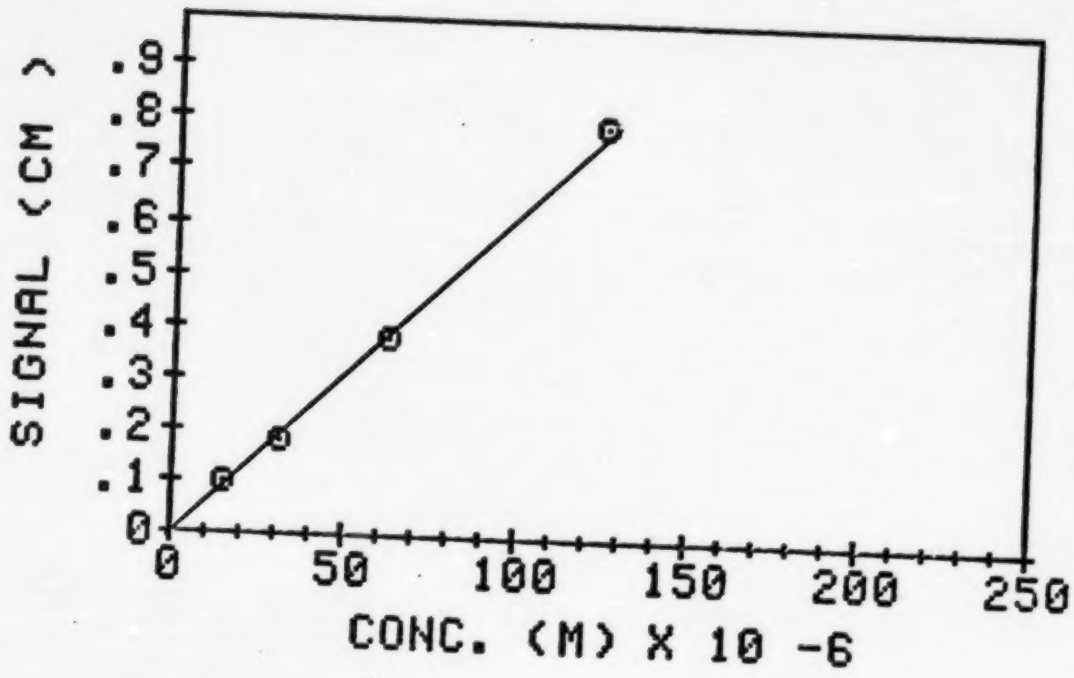


Figure 8. Acetone Azine 290 nm UV Response Calibration



HPLC Analysis of Dansylated Aldehyde Derivatives

Standard solutions of the hydrazine derivatives of acetaldehyde, formaldehyde, acetone, acrolein, propanal, valeraldehyde, and benzaldehyde were prepared. The standard solution of the reagent was 1.12 x 10 -6 M dansyl hydrazine (Pierce Chemical Co.) in acetonitrile. Ten microliters of concentrated HCl was added as the catalyst to 10 ml. of this solution and then a few microliters of the aldehyde was introduced. The solution was allowed to react for 5 minutes with occasional agitation and then a chromatogram was run under the following conditions: flowrate = 1.5 ml/min., 60% acetonitrile/40% water for mobile phase (see Figure 12). The following data was obtained.

Table 13. HPLC SEPARATION OF HYDRAZONE DERIVATIVES

HYDRAZONE OF	RETENTION TIME (MIN)	CONCENTRATION (M)	AREA UNDER CURVE(CM2)
Reagent	1.3	1.12 x 10 -6	.18
	3.2		.80
Reagent + HCl	4.2	2.7 x 10 -2	.24
Acetaldehyde	4.1	3.6 x 10 -3	.93
Formaldehyde	4.4	9.1 x 10 -3	.40
Acetone	4.7	4.1 x 10 -3	.50
Acrolein	4.8	4.5 x 10 -3	.15
Propanal	5.3	2.8 x 10 -3	.62
Valeraldehyde	8.8	2.8 x 10 -3	.53
Benzaldehyde	---	2.9 x 10 -3	---

The peaks at 1.3 min. and 4.2 min were present in every chromatogram. The peak at 1.3 is assumed to be a dansylic acid impurity. The one at 4.2 is believed to be a small amount of the protonated form of dansyl hydrazine in equilibrium with the reagent, formed when HCl is added. The reagent peak disappears (or nearly does) in each chromatogram indicating that the reaction has gone to completion. The benzaldehyde derivative failed to form. It is unclear, at this time, whether this lack of reactivity is a general characteristic of aromatic aldehydes and dansyl hydrazine.

In the above experiments the dansyl hydrazine represented the limiting reagent. The responses observed are then due (if the reaction goes to completion) to a 1 x 10 -6 M solution of the aldehyde. The differing responses observed then represent inherent differences in the response of the different dansyl derivatives of the aldehydes. Using the acetaldehyde derivative it can be estimated that a 10 -6 M solution of the DAIH derivative would give a 0.03 cm2 peak vs the observed 0.93 cm2 peak for the dansyl derivative. The dansyl derivative gives a fluorescence signal about 30 times that for the DAIH derivative.

Figure 9. Acetaldehyde Azine Fluorescence Response Calibration

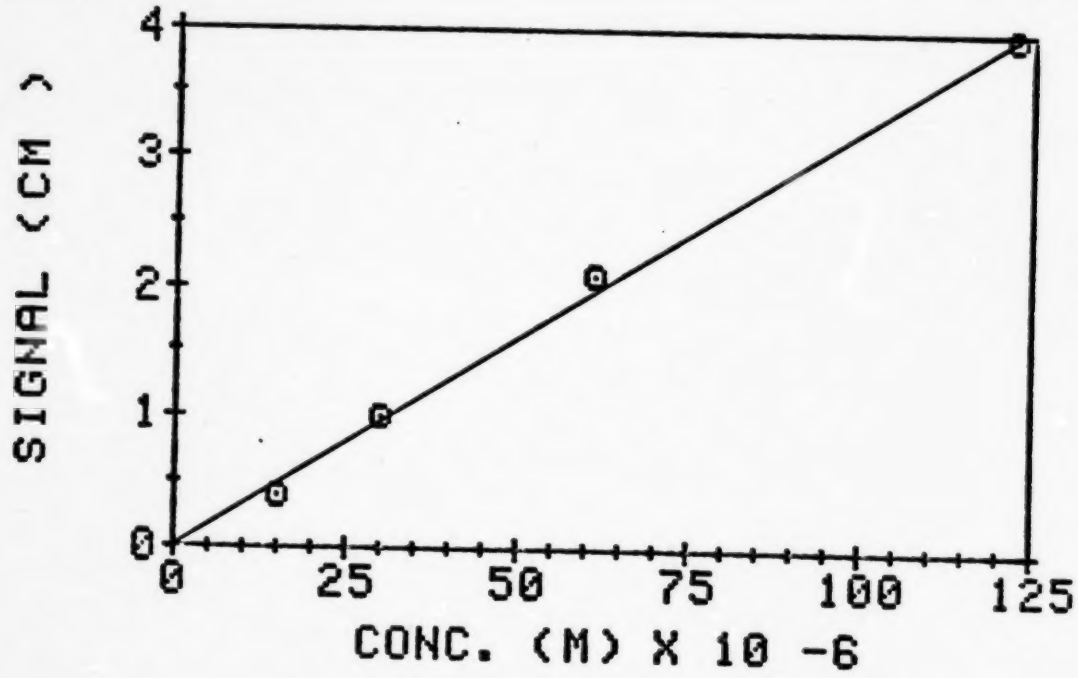


Figure 10. Acetaldehyde Azine 254 nm UV Response Calibration

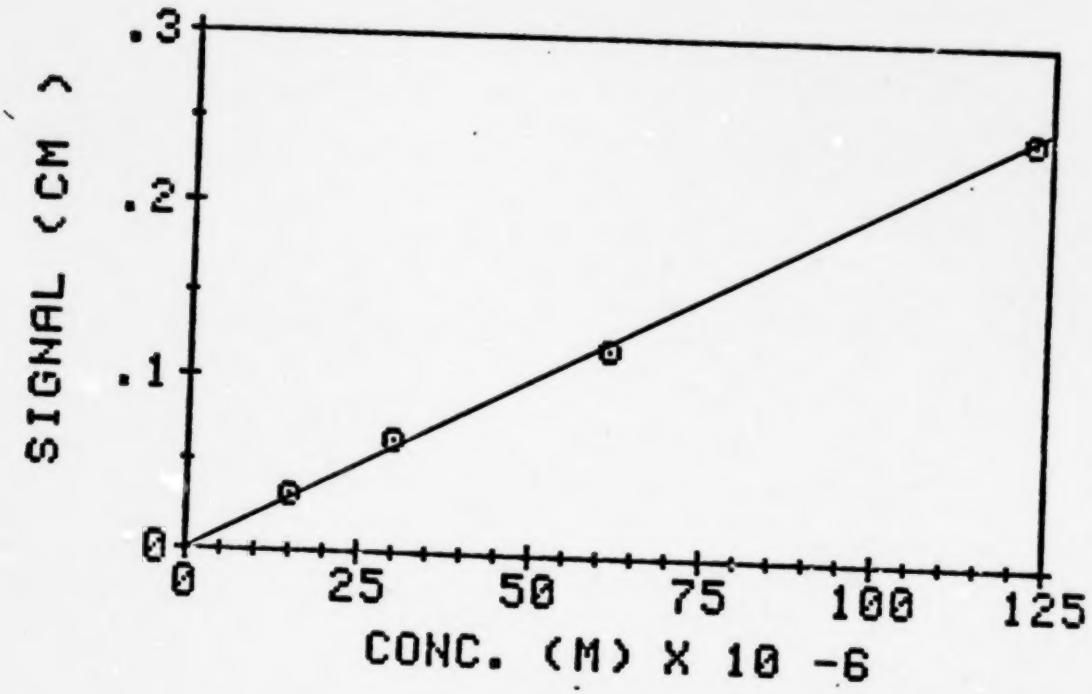
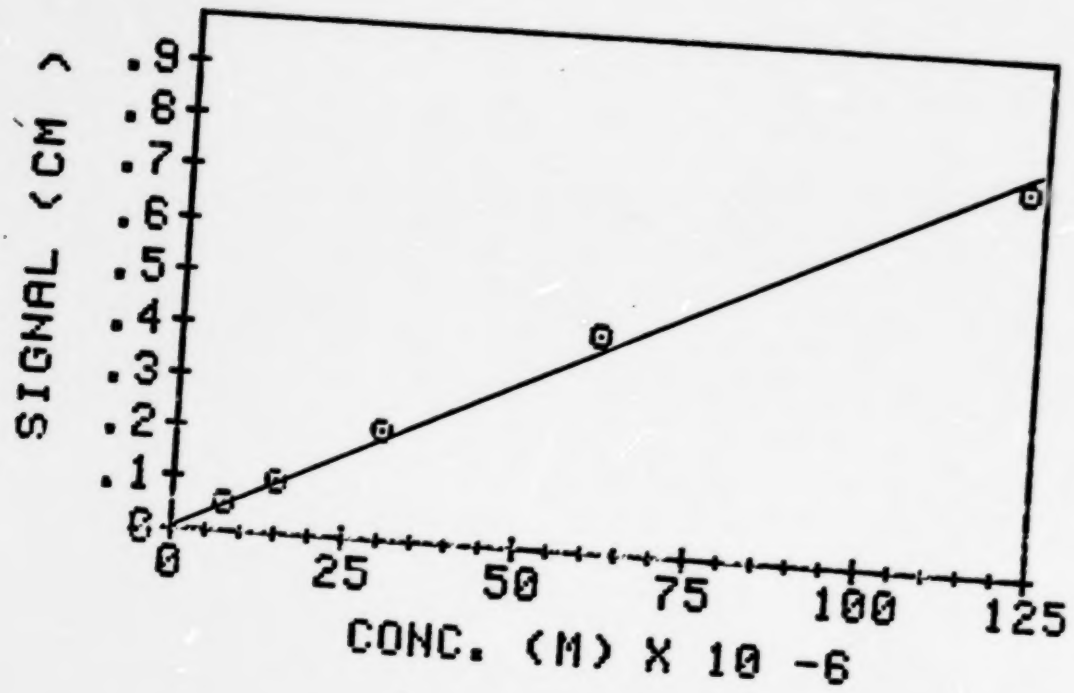


Figure 11. Acetaldehyde Azine 290 nm UV Response Calibration



RESULTS AND CONCLUSIONS

In this chapter the method for determination of aldehydes based on the reaction of 2-diphenyl-1,3-indandione followed by High Performance Liquid Chromatographic separation and fluorescence detection, introduced by Swarin,[9,10,25] was examined. After comparing detection limits for this method with that of ultraviolet absorption analysis at the wavelength of maximum absorption for this fluorescence chromophore, and with that of the DNPH method, this method was found to be inferior. Both the ultraviolet method and the DNPH method were on the order of 25 times more sensitive. Thus, this method was abandoned and an investigation of dansyl hydrazine as a derivatizing agent for HPLC separation, fluorescence detection, and quantification of aldehydes in ambient air was begun.

Although the dansyl hydrazone method is still in a preliminary stage of development, it seems to be inferior chromatographically to the DNPH method. The more complex HPLC separations (overlaps of aldehyde derivatives with the reagent peaks) and the lack of reactivity with aromatic aldehydes (benzaldehyde) suggest that this reagent may require sophisticated HPLC techniques and careful interpretation of the results. Whether the promise of increased sensitivity offered by the dansyl derivatives is realized in practice is still unclear.

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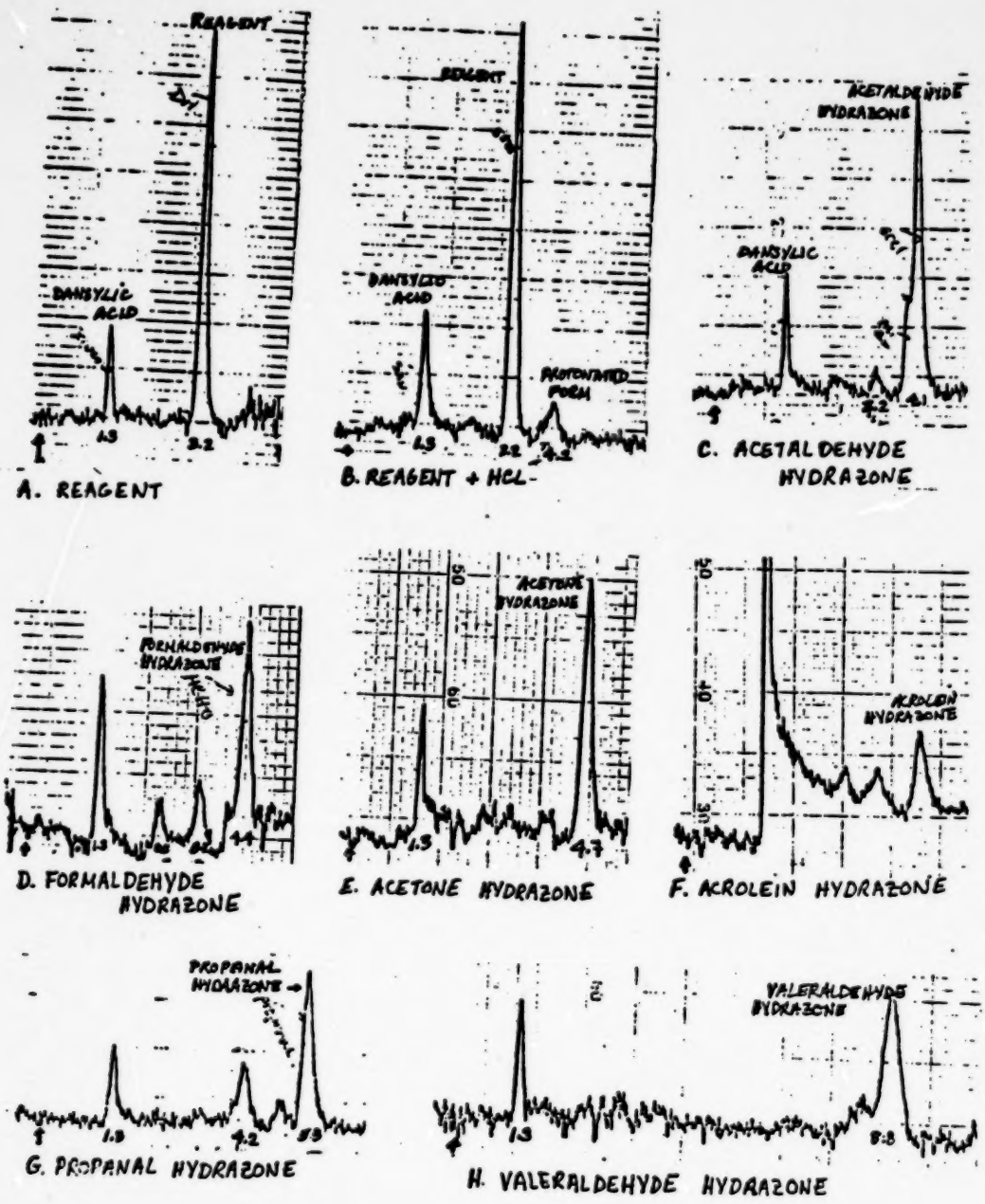

Figure 12. HPLC Separation of Six Dansyl Hydrazones

Chapter 7

Urban and Rural Ambient Air Aldehyde Levels in Schenectady, NY and on Whiteface Mtn., NY

INTRODUCTION

Aldehydes are important atmospheric contaminants produced directly in the combustion of hydrocarbon fuels and indirectly in the atmospheric photodegradation of those same fuels.[39] They play an important role in the production of aerosols and in the modeling of urban atmospheres.[40] Until recently, because of limited analytical techniques, there have been only a few studies of their concentration in the atmosphere. Grosjean et al.[13,41] has reported in detail on the aldehyde concentrations during smog episodes in the Los Angeles area. Kuwata et al.[14] have reported some data on the aldehyde concentrations in Osaka, Japan. Cleveland et al.[42] reported the formaldehyde concentration for four New Jersey cities. There are no studies of aldehyde concentrations (other than formaldehyde) in smaller urban areas or regions that would be expected to have very low or "background" concentrations of aldehydes. For formaldehyde there have only been a few such studies.[43] Further work is necessary to provide information for setting the initial conditions for regulatory models. This work is intended to provide some of that information.

EXPERIMENTAL

Using a previously described analytical technique[7] two projects were undertaken. In the first of the projects the air in Schenectady, N.Y. was monitored daily. The second project consisted of sampling at the State University of New York at Albany's (SUNYA) Atmospheric Sciences Research Center (ASRC) on Whiteface Mtn. in Wilmington, N.Y. over the period of about a week.

In the Schenectady work the sampling was done through a glass tube extending outside the third floor of the Science and Engineering building on the Union College campus. The campus is located in the middle of an urban area and is surrounded on two sides by busy city streets. The other two sides are more lightly traveled thoroughfares. The S. & E. building is centrally located on the campus and is therefore about a third of a mile from the nearest city street. There are no city streets extending onto the campus, although there are roads that provide access to parking lots around the periphery of

the campus.

The sampling was done as described in the previously published description of the technique[7] with the exception that the sample volume at the end of the sampling was adjusted to 4.0 ml. instead of 2.0 ml. The volume of air sampled was 90.0 liters over a period of three hours. Sampling was done twice a day, from about 9:00 AM to 12:00, and from about 1:00 PM to 4:00. The samples were analyzed within a day.

Data on rural aldehyde levels were obtained at the SUNYA ASRC on Whiteface Mtn. in Wilmington, NY. Wilmington is located in a rural portion of New York State approximately 100 miles from a city of any substantial size. The area is mountainous and in the midst of the Adirondack State Park. The sampling station is located on top of the 4900 ft. mountain about 300 ft above the road to the top. Access to the road is limited and the traffic is minimal. Other work done at the center has indicated that the air at the station is not significantly affected by the road or local traffic. The samples were taken off a three-inch diameter pipe that extended above the roof of the station. The takeoff for the sampler was located upstream from a high volume sampler that drew air through the pipe at a rate of 100 liters/minute. Samples were taken several times each day in the same manner as described above and refrigerated. The analyses were done the day following our return to Schenectady, a delay of at most one week from when the samples were taken.

The solutions were analyzed with a Varian 5020 HPLC with a Tracor 970A variable wavelength detector using an Alltech RP-C18 25 cm column. The analysis of each sample was done isocratically (60/40 acetonitrile / water, 1.5 ml/min) with the uv detector at 360 nm.

The analysis of the C_3 compounds was not possible because of the ubiquitous contamination of reagents and solvents with acetone. The contamination level amounts to roughly a 4.0 ppb sampling equivalent. The other C_3 compounds were all considerably below that limit.

In order to establish some analytical criteria, blank samples were analyzed according to a recommended literature procedure to determine the standard deviation of the analysis of the blanks[19] (see Chapter 3 for additional information). A compound was considered to be detectable if the analysis exceeded three times the standard deviation and to be in the region of quantification if it exceeded ten times the standard deviation. For formaldehyde those limits are 0.10 ppb (detection) and 0.32 ppb (quantitation) and for the other

low molecular weight aldehydes (with the exception of the C_3's) 0.16 ppb (detection) and 0.53 ppb (quantitation).

RESULTS AND DISCUSSION

Figure 13 shows the results of the formaldehyde analyses in the Schenectady work. In order to reduce the scatter, daily and adjacent day average values are shown. All the data taken was in the quantification range and went from a low of 0.70 ppb to a high of 30.5 ppb, with an average daily concentration of 7.6 ppb (4.9 ppb was the standard deviation of the average value). Although there is a large variation in the daily data there was apparent, over the course of the summer, a general trend toward lower formaldehyde concentrations. It is not clear what might be causing the overall downward trend in formaldehyde levels.

The data on acetaldehyde is much more sparse. Few samples had levels that were significantly above reagent blank levels. In Table 14 is given a frequency distribution of the concentrations of formaldehyde and acetaldehyde.

The concentration of acetaldehyde was always significantly below that of formaldehyde. When the amount of acetaldehyde was detectable, the ratio of formaldehyde to acetaldehyde averaged about 14:1. Since acetaldehyde was, for the vast majority of samples, below its detection limit of 0.16 ppb the average ratio, for those samples, was greater than 48:1 (the average daily concentration of formaldehyde, 7.6 ppb, divided by the detection limit for acetaldehyde). A weighted average would make the upper limit for the ratio 44:1 (for all the samples).

The variation of the formaldehyde over the course of the day was explored by sampling every three hours over a 36 hour period. The results of that work are given in Figure 14. There are two peaks in the formaldehyde concentration over the course of the day. The first occurs about 7:00 - 10:00 AM and the second about 6:00 - 10:00 PM. The peaks seem to be clearly correlated with commuting automobile traffic. The daily minimum occurs at about 3:00 AM. Over a 24 hour period the range of formaldehyde concentrations was 1.7-8.1 ppb, a factor of slightly less than five.

The work at the SUNYA ASRC station was done over a period of one week (8/14-20/83). The weather preceding the week of sampling had been rainy. The week began with clear cool days and it got progressively warmer and more humid. The week ended with a brief light shower. The temperature at the top ranged from about 52^{o}-64^{o}F. Wind

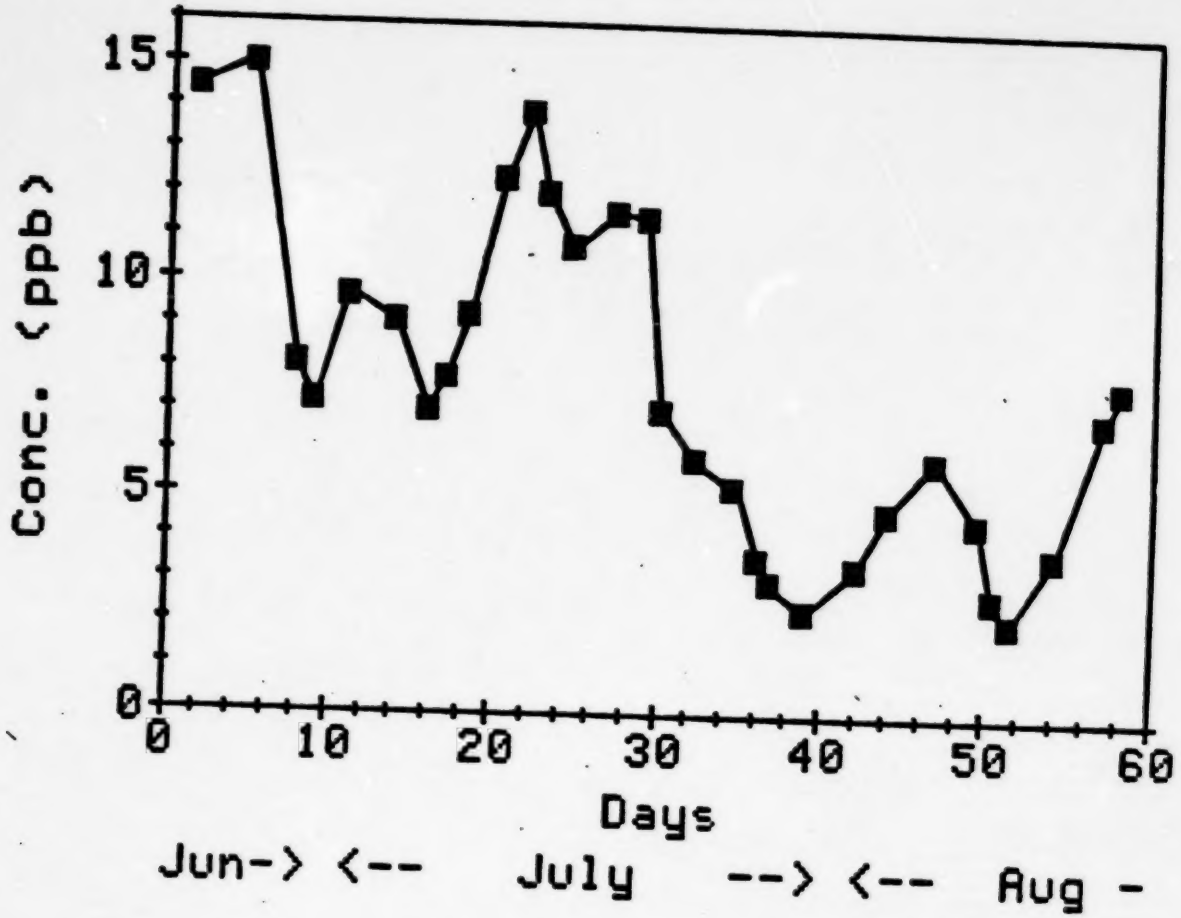

Figure 13. Daily and adjacent day averaged formaldehyde concentration for Schenectady, NY, June-August, 1983.

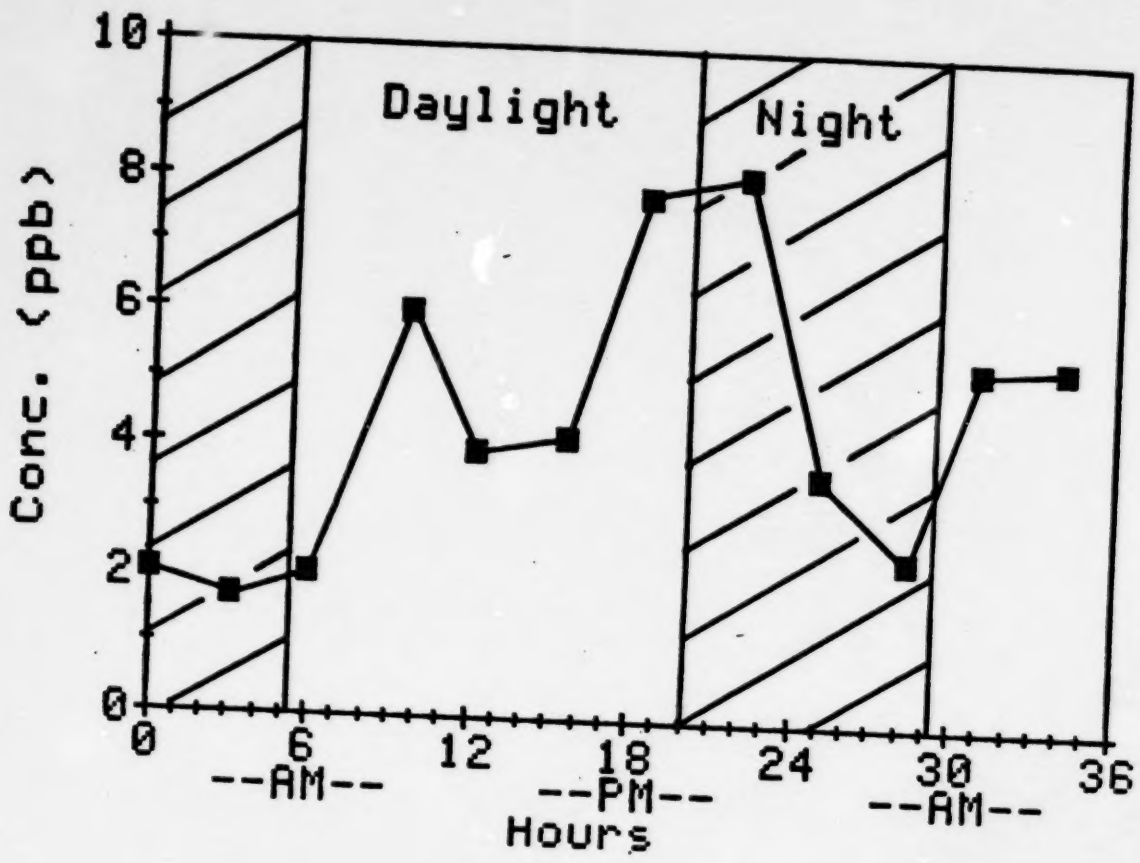

Figure 14. Diurnal variation of the formaldehyde concentration in Schenectady, NY.

direction, temperature and ozone concentrations were recorded from the routine monitoring devices installed at the station.

Table 14 presents the frequency distribution for the Whiteface data. No significant quantities of any other aldehydes, besides formaldehyde and acetaldehyde, were detected. The data are plotted in Figure 15. The formaldehyde concentrations range from 0.6-2.6 ppb, the acetaldehyde from below our detection limit (0.16 ppb) to a barely measurable 0.80 ppb. Most of the acetaldehyde data, above the detection limit, is in the "detected" range (0.16-0.53 ppb) but cannot be considered as quantified. From Figure 15 it is apparent that there is a tendency for the aldehydes to rise and fall with the ozone. The data generally support the notion that whatever produces ozone also produces formaldehyde.

Figure 16 provides a more detailed look at the formaldehyde concentrations as a function of time of day. Over a two day period samples were collected at three hour intervals. The period sampled over corresponds to an increase in ozone concentration from about 30 ppb to 97 ppb. Over that period there was also a general increase in the formaldehyde. Nonetheless it is still possible to discern a roughly 24 hour cycle in the formaldehyde concentration. The values peak at hours 10 and 34, then give minima at hours 26 and 48. The maxima are at about 10:00 - 12:00 in the evening and the minima are at about 12:00 - 2:00 in the afternoon. Presumably the pattern reflects the fact that the chief mechanism for loss of formaldehyde is photolysis. Thus the afternoon minimum in its concentration. The evening maxima is probably a reflection of the absence of a photolysis sink but formaldehyde's continued production from the reaction of hydrocarbons with ozone.

Not unexpectedly the formaldehyde levels observed at Whiteface were significantly less than the levels in Schenectady. During the same week the work was performed at Whiteface the levels of formaldehyde in Schenectady averaged 6.7 ppb and ranged from 3.2-9.5 ppb. Schenectady is about 90 miles south of Wilmington, N.Y. and during that week was influenced by the same weather systems. The average level of formaldehyde at Whiteface was about 1.3 ppb and, as mentioned earlier, ranged from 0.6-2.6 ppb. The levels differed by roughly a factor of five.

The acetaldehyde data is difficult to interpret with any certainty. The amount of data from each of the locations is limited, and what data there is, tends to be in the range that is not quantitative. There is however some indication that the acetaldehyde, when detectable, is at about the same level on Whiteface Mtn. as in

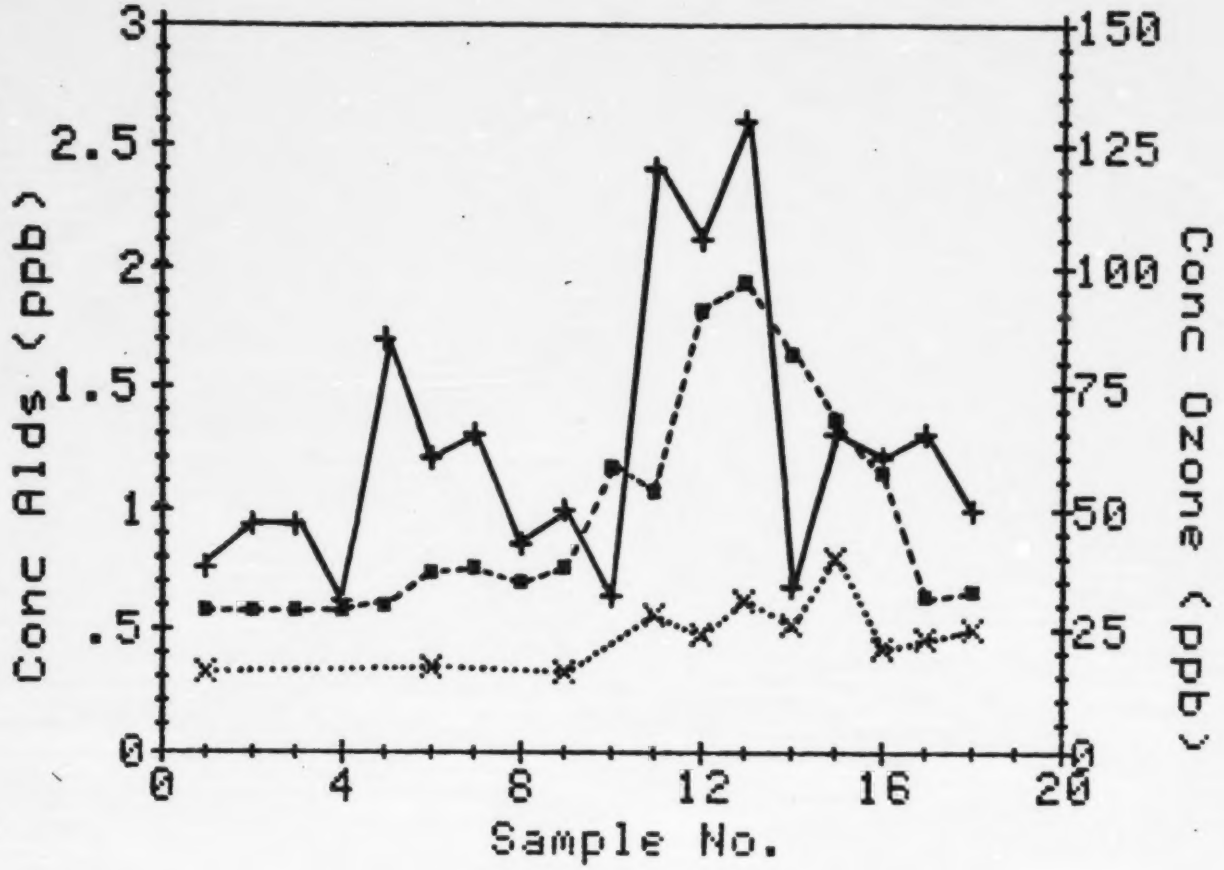

Figure 15. Relation of the ozone conc. (dashed line, small squares) to the concentration of formaldehyde (solid line, +'s) and acetaldehyde (dotted line, x's) on Whiteface, Mtn., Aug. 14-20, 1983.

Schenectady, N.Y.

A comparison of the above data with Grosjean's data from Los Angeles[13,41] indicates significantly lower levels of aldehydes. It also appears that there may be a fundamental difference in that the higher aldehydes are absent from the Schenectady and Whiteface data. For Los Angeles over 40% of the samples had levels above 20 ppb in formaldehyde whereas only a single sample (1%) had a comparable level in Schenectady. The percentage of samples with acetaldehyde above 5 ppb in Los Angeles was 46%, while there were no samples with levels that high in Schenectady. The majority of the Schenectady data (11 out of the 16 samples) was less than 1 ppb in acetaldehyde.

Table 14. Frequency Distribution of Concentrations

a. Schenectady, N.Y.

H2CO (ppb)	# Samples(%)	CH3CHO (ppb)	# Samples(%)
ND *	0	ND	55 (77)
0-10	56 (79)	0-1	11 (15)
>10-20	14 (20)	1-5	5 (8)
>20	1 (1)	>5	0 (0)

b. Whiteface Mtn., N.Y.

H2CO (ppb)	# Samples(%)	CH3CHO (ppb)	# Samples(%)
ND	0	ND	7 (39)
0-10	18 (100)	0-1	11 (61)
>10-20	0	1-5	0 (0)
>20	0	>5	0

* ND-Not Detected

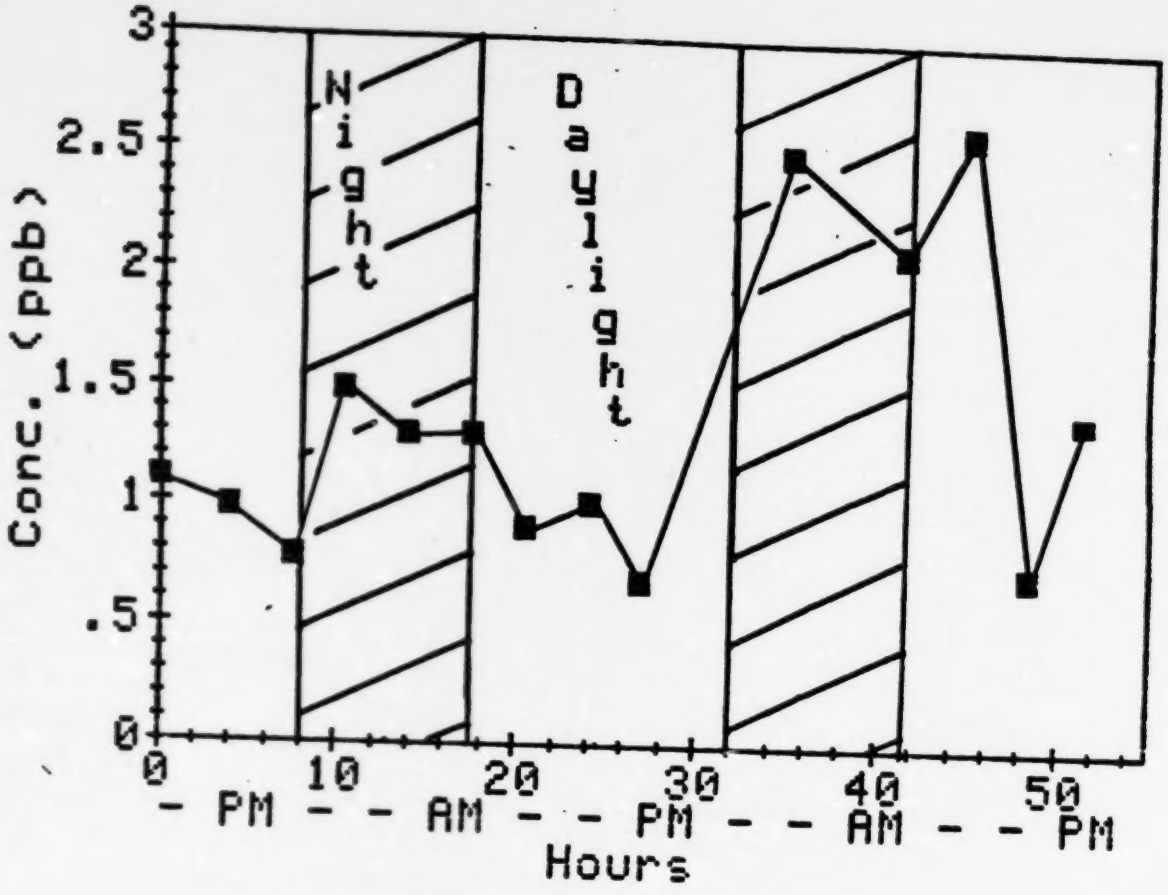

Figure 16. Diurnal variation of the formaldehyde concentration on Whiteface Mtn.

Chapter 8

Cartridge Sampling

INTRODUCTION

In 1983, Kuwata reported a revised technique for assaying air for carbonyl compounds based on the derivatization of aldehydes with DNPH[14]. The method allows for sampling with a C18 cartridge impregnated with a DNPH-acetonitrile phosphoric acid mixture. The acetonitrile is removed by evaporation. Air is drawn through the prepared cartridge and then the cartridge is leached out with a small volume of acetonitrile. The leachate is analyzed by HPLC in the standard fashion. The technique not only promises a simplified procedure, but it also has the potential of increasing sensitivity.

The following describes some preliminary experiments involving the testing and use of the cartridge sampling.

EXPERIMENTAL

Cartridge Preparation:

The Sep-Pak C18 cartridges (Waters Associates, Milford, MA) were prepared for sampling by first washing each cartridge with 2 ml of acetonitrile. The cartridges were then saturated with 2 ml of a 0.2% DNPH and 1% phosphoric acid solution in acetonitrile at a rate of 2 ml/min. Next, they were dried under reduced pressure in a nitrogen atmosphere. The apparatus consisted of a descicator with both an inlet and an outlet. A nitrogen stream (20-30 ml/min) was connected to the inlet. The outlet was attached to an aspirator. The cartridges were dried for 1 hour under these conditions and then connected directly to a nitrogen stream (50-100 ml/min) for an additional 30 minutes. The prepared cartridges were capped with glass rods and stored in nitrogen containing-brown jars at 3-5 degrees.

Cartridge Sampling:

Sampling with the SP cartridges is very similar to sampling with impingers, rather than two impingers there are two cartridges in series. Air is drawn through the cartridges at about 0.5 l/min. For atmospheric sampling about 45 l of air is drawn through the cartridges. Upon completion of sampling, the hydrazones are eluted from the cartridge by 2.0 ml of acetonitrile. Sampling with cartridges is performed in one direction and elution with solvent in the opposite direction.

An aliquot of the eluent is then injected into the HPLC for analysis in the usual way.

Cartridge Testing:

A comparison of the cartridge results with that of the impinger DNPH-ACN method was performed for formaldehyde. A Metronics Dynacalibrator with a formaldehyde permeation tube was used to generate a series of concentrations of formaldehyde (0.12-1.5 ppm). A 'Y' connector was used to connect both the impinger pump and the cartridge pump to the formaldehyde source. After sampling the impinger solutions were worked up in the usual way and the cartridges were worked up as described above. The analysis of the resulting acetonitrile solutions was performed in the usual way also and the standards previously developed were used for calibration.

RESULTS AND DISCUSSION

The results (Figure 17 and Table 15) were very encouraging with formaldehyde. Not only were the values for each dilution run comparable, but it appeared that the cartridge technique was more efficient since the chromatograms for the second cartridge in series of two were cleaner than the chromatograms for the second of the two impingers. The average absolute error was about 7% and there appeared to be no systematic bias.

Table 15. Comparison Between The Impinger And Cartridge Techniques for Formaldehyde

Cartridge (ppm)	Impinger (ppm)	% Difference
1.55	1.50	+3
0.83	0.78	+6
0.23	0.26	-10
0.15	0.16	-6
0.13	0.12	+8

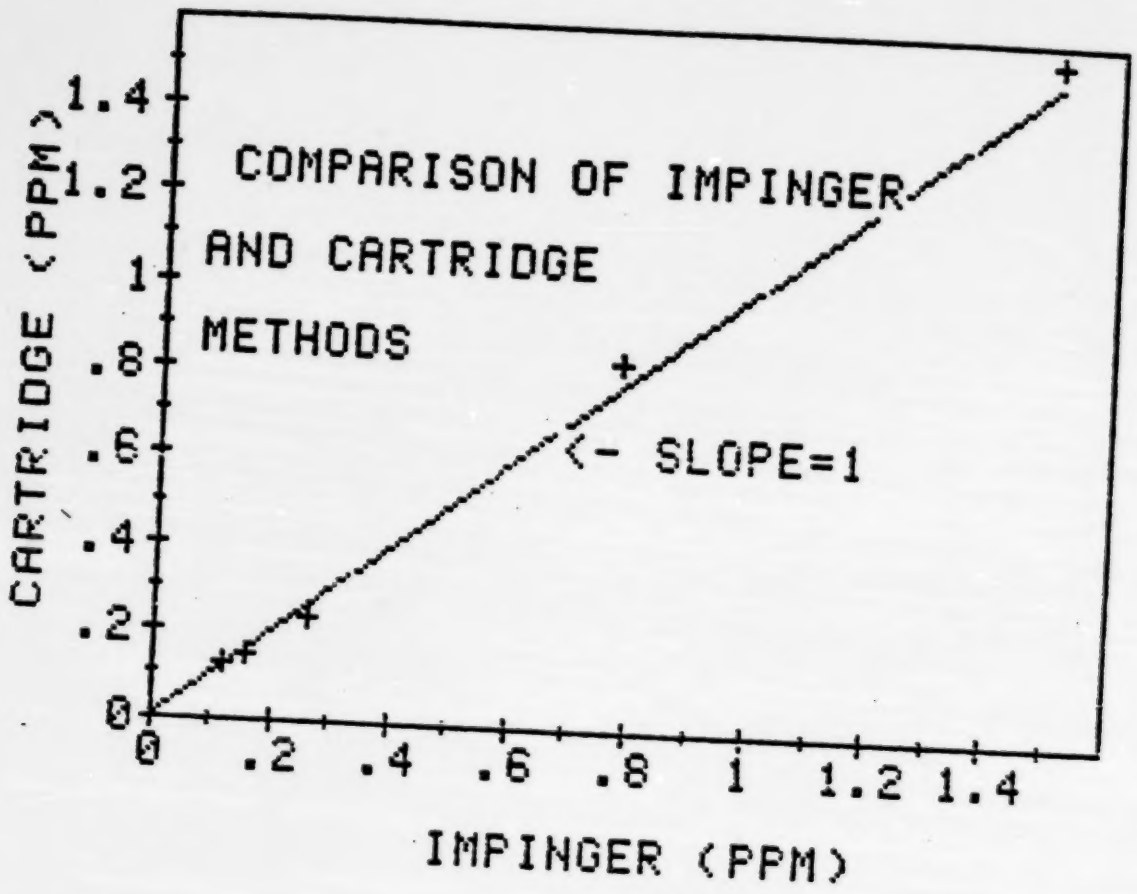

Figure 17. Comparison of the impinger and cartridge techniques in sampling formaldehyde.

Chapter 9

Cloudwater Sampling[44]

For the past decade or so, aldehydes and ketones have been recognized as important intermediates in photochemical smog and we discussed several methods earlier for their determination. Much less work has been done on determining aqueous phase concentrations of these carbonyl compounds. Work that has been done in this area, generally, has been specific for formaldehyde levels only. It would be desirable to be able to apply the selectivity and efficiency of the DNPH method to aqueous determinations.

Water creates a natural interference in the reaction between DNPH and carbonyl compounds, as shown by the equilibrium below:

DNP-NHNH2 + RCH=O -----> H2O + RCH=NNH-DNP

If the concentration of the water in the reaction mixture is kept to a minimum, the interference, can be minimized. Recently, Grosjean and Wright attempted to use an aqueous DNPH reagent for determination of carbonyl compounds in urban water.[45] A slightly different approach was used independently by us during July-August, 1984 for aldehyde and ketone determinations in cloud water at the State University of New York at Albany's Atmospheric Sciences Research Center (ASRC) atop Whiteface Mountain in the Adirondacks of New York State.

EXPERIMENTAL

Reagent Testing:

Three reagent solutions were tested for efficiency and stability. The first reagent (listed below) was an aqueous solution and the other two were acetonitrile solutions of DNPH.

A) 0.5g DNPH and 53.5ml H3PO4 in 500ml water
B) 0.2% DNPH and 1% H3PO4 in acetonitrile
C) 0.5g DNPH and 0.1% H2SO4 in acetonitrile

In addition to direct analysis of the solutions resulting from the addition of A-C to the water sample, an extraction of the DNPH-aldehyde derivatives from the aqueous solution resulting from the use of (A) was tried. To 2.0 ml of the aqueous aldehyde solution was added 1.0 ml of solution (A). The final 3.0 ml was then injected through a SEP-PAK C18 cartridge (Waters Associates) in

order to extract out the DNPH derivatives from the water. This cartridge was then leached with 2.0 ml of acetonitrile, and the resultant solution was then analyzed by HPLC as described later. As a standard for comparison, solution 2.5 ml of (C) and 0.5 ml of the aqueous aldehyde solution were used. This ratio, from the work of Kuntz et al, produced negligible water interference for the aldehydes.[7] The acetonitrile solution (B) was the same as the one Kuwata used for his preparation of cartridges for ambient air analysis.[14] Tests were performed on aqueous solutions of formaldehyde and acetaldehyde.

Sampling Work:

Samples were taken directly from the cloud water collectors atop ASRC's Whiteface Mountain field station every one to two hours during a cloud cover event when collection was possible. A 1.5ml aliquot was added to 0.5ml of the reagent solution (A) or (B). There was a maximum delay time of 10 minutes from the time of impact on the collector until addition to the reagent. The resultant solutions were then refrigerated until transport to Union College. The maximum delay time between reagent mixing and analysis was five days with the majority of analyses being done within two days. Analysis was done on a Varian 5000 HPLC equipped with a 254nm uv detector and connected to a Tracor 970A variable wavelength detector for monitoring at 360nm. Samples were run isocratically at 65%/35% ACN/H20 at a flow rate of 1.5 ml/min on a 25cm x 4.6mm 10 micron Alltech C18 column.

DISCUSSION

Table 16 shows the change in analysis for the three reagents and the cartridge extraction with time. As can be seen the aqueous reagents showed significant changes in the concentration of the aldehydes over the test periods. For practical reasons solution (B) was ultimately chosen for analysis. The stability of the actual cloud water samples was also determined. Four samples taken during an event on 7/11 using solution (B) were run on 7/13 and again on 7/23. The results are shown in Table 17.

The stability of these solutions was crucial for this project because the samples needed to be stored and transported from Wilmington, N.Y. to Schenectady, N.Y. For this reason and because of the greater efficiency, the acetonitrile solution (B) was used instead of the aqueous solution for derivatization from event #4 until the end of the project. Samples taken prior to this used the solution (A) and the results are questionable. All samples taken using the acetonitrile solution yielded

Table 16. PERCENT CHANGE IN CONCENTRATION WITH TIME: COMPARISON OF WATER AND ACETONITRILE DNPH REAGENTS

DNPH Reagent	Formaldehyde	Acetaldehyde	Time (Days)
H_3PO_4/H_2O	-91%	-94%	7
H_3PO_4/H_2O (Cart.)	-34%	-34%	7
H_3PO_4/ACN	-13%	-7%	5
H_2SO_4/ACN	-5%	-12%	7

Table 17. STABILITY OF FIELD SAMPLES

Sample #	Date	Formaldehyde Conc. (uM)	Acetaldehyde Conc. (uM)	Acetone Conc. (uM)
1	7/13	2.08	0.38	0.76
	7/23	2.48	NM	NM
2	7/13	1.63	0.54	0.99
	7/23	1.56	0.35	0.99
3	7/13	0.89	0.47	0.74
	7/23	1.33	NM	0.86
4	7/13	2.37	0.86	NM
	7/20	2.21	0.52	1.44
	7/23	1.91	0.62	1.27

quantifiable results above blank levels.[19]

For the samples taken on Whiteface, there were consistently only three carbonyl compounds present. Occasionally, there were other peaks which have not yet been identified. The results of the work are summarized in Table 18. The Table shows the concentrations of the carbonyl compounds for each event sampled. Average concentration is given along with the range for each compound during each event. In some of the samples one or more of the compounds was not detectable and these were not counted for the average of that particular compound. In general, none of the compounds displayed great fluctuation in concentration, as shown by the range for each event. While formaldehyde was present in the highest concentrations, both acetaldehyde and acetone were usually present at comparable levels. The greatest fluctuations are between events, the concentrations during a single event showed little variation.

The consistency of these results is interesting from the point of view of transport, production, and breakdown of these compounds in the atmosphere. Grosjean and Wright report the presence of several higher aldehydes in urban atmospheric water.[45] The levels are comparable to those found on Whiteface, a rural site. However, they used an aqueous solution for derivatization. We found the DNPH derivatives to be unstable in our aqueous solution. The concentrations they report are therefore questionable, but the qualitative presence of these compounds seems certain.

During the period of our sampling, the prevailing winds brought air to Whiteface from the west, often from the Great Lake region but occasionally from both Canada and also from the south. Grosjean and Wright suggest that the clouds act as excellent scavengers of the airborn carbonyl compounds.[45] Assuming that these clouds are then transported from urban to rural areas, our data suggests that something happens to these compounds that is selective for the higher aldehydes and ketones. A simple model might be the following: the aldehydes and ketones are produced by exhaust and factory emission and exist mostly in the gas phase as opposed to the solid aerosol.[46] These are then scavenged from the gas-phase by cloudwater droplets. Once in the aqueous phase they can undergo chemical decomposition, chemical reaction, or they may be washed out by rain. The fact that similar levels of only the simple aldehydes are found on Whiteface suggests that either there is a natural means of replenishment for these compounds whereby they exist in a steady state with natural or urban hydrocarbons or the simple aldehydes seen are the degradation products of the higher aldehydes transfered from urban areas. The

Table 18. CLOUDWATER CONCENTRATIONS OF CARBONYL COMPOUNDS ON WHITEFACE MOUNTAIN, JULY-AUGUST, 1984

Date (Event #)	Compound	Ave Conc (uM)	Range	# of[a] samples
6/24-6/25 (1)	Form.	3.29	1.78-5.52	15/15
	Acetald.	1.15	0.85-1.64	6/15
	Acetone	13.53	1.10-133.38[b]	15/15
6/27-6/28 (2)	Form.	2.27	1.78-3.08	10/10
	Acetald.	0.56	0.44-0.70	10/10
	Acetone	1.00	0.54-1.31	10/10
7/4-7/5 (3)	Form.	5.11	3.21-14.8	10/10
	Acetald.	1.52	0.64-3.10	5/10
	Acetone	1.76	1.06-3.60	9/10
7/11-7/12 (4)	Form.	1.43	0.36-2.37	16/16
	Acetald.	0.51	0.28-0.86	5/16
	Acetone	0.83	0.74-0.99	3/16
7/23 (5)	Form.	2.46	1.94-3.72	5/5
	Acetald.	0.68	0.32-1.02	4/5
	Acetone	0.98	0.52-1.29	3/5
7/27-7/28 (6)	Form.	2.36	1.08-3.86	7/7
	Acetald.	0.64	---	1/7
	Acetone	4.45	2.41-6.28	7/7
8/1-8/2 (7)	Form.	1.85	1.14-2.46	8/8
	Acetald.	0.66	0.43-0.79	4/8
	Acetone	0.64	0.61-0.68	3/8
8/7 (8)	Form.	2.02	0.62-3.77	7/7
	Acetald.	0.43	0.33-0.72	4/7
	Acetone	0.51	0.43-0.58	2/7
8/9-8/10 (9)	Form.	3.30	2.32-4.08	8/8
	Acetald.	0.65	0.28-1.64	7/8
	Acetone	0.78	0.32-1.04	3/8

[a] Number of Quantifiable/Total Number of Samples
[b] Likely contamination

hydrocarbons then serve as sources of the carbonyl compounds and the particulate matter with further oxidation (degradation) and washout providing sinks for the carbonyl compounds. This is supported by the data which shows a surprisingly small range of concentrations not only throughout any given event but also throughout the entire summer for each of the three compounds. It would be interesting to determine the fate of these compounds at different stages of transport.

Chapter 10

Conclusions and Recommendations

The following general conclusions and recommendations result from this work and the evaluation of the literature.

1. The DNPH method of trapping and quantifying the levels of aldehydes in ambient air appears to be efficient and accurate.[8,10,47]

2. It has been shown not to be sensitive to interferences by common atmospheric contaminants.[11-13]

3. Methods based on other hydrazine chromophores (DIAH and dansyl hydrazine)[9,10,25,48] appear to offer no substantial advantages over DNPH while suffering from more difficult and longer analyses and inefficiencies in derivatization.[48]

4. An Alltech C-18 RP HPLC column is recommended for rapid, efficient analytical separations of the C1-C4 aldehydes.[49]

5. The DNPH reagent is stable when kept in glass or teflon capped glass containers for up to four weeks. If no acid is added to the reagent it appears to be stable for several months. It is recommended that acidified reagent be used within two weeks.[50]

6. The sampled reagent appears to be stable for at least three weeks after sampling with refrigeration.[50] It is recommended that analyses be performed within two weeks of sampling and that the samples be stored in teflon sealed vials under refrigeration.

7. The limits of detection and quantification for the DNPH method are such that formaldehyde is readily determinable even in "clean" air but information on the other carbonyl compounds may be limited to urban (less "clean") areas.[50,51]

8. Analysis of dicarbonyl compounds with the DNPH method will require special care because of the extreme insolubility of the di-DNPH derivatives.[52] In particular sampling times will have to be carefully adjusted based on anticipated concentrations so as not to exceed the solubility limits for the derivatives. In addition the HPLC analysis should be done at higher ACN levels than the standard analysis to avoid column precipitation and to shorten the

retention times.[52]

9. The uv detection of the derivatives should be done at 360 nm but the 360/254 area ratio may aid in the determination of the nature of unknown materials and serve to confirm identifications made on the basis of retention times.[52]

10. More work needs to be done in smaller cities and rural areas to provide additional information on "background" levels of aldehydes.[51] The information would be of use in urban atmospheric modeling as initial conditions.[40]

11. Although the DNPH-acetonitrile method is useful for the determination of aldehyde levels where there are laboratory facilities available, it is inconvenient for field sampling. The necessity of handling a volatile, flammable, regulated organic solvent limits the kinds of situations suitable for DNPH-acetonitrile sampling.[51]

12. Preliminary testing of a DNPH cartridge technique[14] has shown it to be accurate and more convenient than solvent based alternatives.[53] It is recommended that future work be devoted to use of DNPH cartridge sampling for aldehyde determinations.

13. DNPH acetonitrile reagent solutions with subsequent HPLC analysis may prove useful for rain and cloudwater sampling for aldehydes. The preliminery work reported here[54] indicates that the levels of acetaldehyde and acetone are comparable to that of formaldehyde.

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